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DEVELOPMENT OF SPACE STABLE THERMAL  
CONTROL COATINGS FOR USE ON LARGE  
SPACE VEHICLES

National Aeronautics and Space  
Administration  
George C. Marshall Space Flight Center  
Huntsville, Alabama 35812

Prepared by

J.E. Gilligan

with contributions from

Y. Harada  
C. Giori  
F. Jarke  
G.A. Zerlaut

of

IIT Research Institute  
Technology Center  
Chicago, Illinois 60616

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FOREWORD

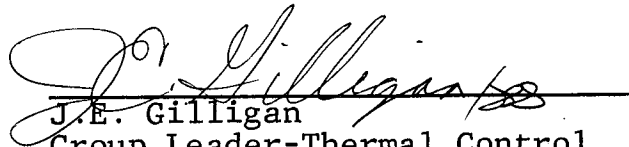
This is Report No. IITRI-C6233-20 (Triannual Report) of IITRI Project C6233, Contract No. NAS8-26791, entitled "Development of Space Stable Thermal Control Coatings for Use On Large Space Vehicles." This report covers the period from May 1 through August 31, 1972.

Major contributors to the program during this period include: Mr. J.E. Gilligan, Project Leader; Mr. Y. Harada and Mr. W. Logan, Pigment Manufacturing Studies; Dr. Claudio Giori, OI-650 improvement; Mr. F.O. Rogers, paint preparation; Mr. Robert F. Boutin, irradiation experiments and reflectance measurements; and Mr. Gene A. Zerlaut, general consultation and administrative management.


The work reported herein was performed under the technical direction of the Space Sciences Laboratory of the George C. Marshall Space Flight Center; Mr. Daniel W. Gates acted as the Project Manager.

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Respectfully submitted,  
IIT RESEARCH INSTITUTE

  
J.E. Gilligan  
Group Leader-Thermal Control  
Polymer Chemistry Research

APPROVED:

  
G.A. Zerlaut  
Manager  
Polymer Chemistry Research

JEG:jss

IIT RESEARCH INSTITUTE

## ABSTRACT

The development of a large scale manufacturing method for the production of a stable zinc orthotitanate pigment has been under intensive investigation. The efforts to improve Owens-Illinois 650 Glass Resin as a paint vehicle have been successful. Furthermore, paints prepared from the resin pigmented with silicated ZnO have shown the greatest resistance to ultraviolet irradiation of any system evaluated during the course of our several years of investigations on satellite radiator coatings. (This system has been engineered to the point where its use on flight hardware<sup>2</sup> is warranted.)

EPR investigations have continued, and results on several pigments are reported. Three series of ultraviolet irradiation tests of pigments and paints have been completed, and analysis of these results are also reported.

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Report No. IITRI-C6233-20  
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DEVELOPMENT OF SPACE STABLE THERMAL  
CONTROL COATINGS FOR USE ON LARGE SPACE VEHICLES

1. INTRODUCTION

The research effort in passive spacecraft temperature control has, historically, been concentrated on the development of the class of surfaces known as solar reflectors - that is, surfaces with high reflectance for solar radiation and with high emittance in the thermal (infrared) spectrum. Basically, these surfaces must be stable in the total environment that they will experience. This requirement means that once we have achieved a high level of intrinsic stability of these materials in the laboratory we must be able to produce them in large quantities, and we must make certain that this stability is preserved in the process and will exist and can be protected in the entire pre-launch environment as well. Applications on large space vehicles, therefore, present new R&D problems - not simply traditional ones in greater dimensions.

The program consists of four major tasks: pigment development, binder development, environmental effects evaluations, and general coatings investigations. The relative emphasis in each of these tasks varies according to the urgency of the problems elucidated in our investigations, and, of course, with the availability of time and funds. Our efforts have been expended mainly on the development of a pigment manufacturing method; binder development; environmental testing and evaluation activities are also continuing.

## 2. PIGMENT PRODUCTION DEVELOPMENT

### 2.1 Introduction

The purpose of this effort is to develop a method of producing zinc orthotitanate ( $\text{Zn}_2\text{TiO}_4$ ) thermal control pigments which will be rapid, possess a high yield, and will produce in large quantities a space-stable product. Several methods are under investigation, each potentially capable of manufacturing greater amounts of  $\text{Zn}_2\text{TiO}_4$  at a lower cost than the existing laboratory synthesis processes. The goal of this effort is to achieve a batch production rate of 10 pounds or more of a stable zinc orthotitanate.

Production methods to be investigated are coprecipitation, reaction sintering, and heat treatment.

#### 2.1.1 Coprecipitation

This method involves the deposition of an intimate zinc salt-titanium salt mixture by coprecipitation and the firing of this product at relatively low temperatures ( $600^\circ\text{--}1000^\circ\text{C}$ ) to produce  $\text{Zn}_2\text{TiO}_4$ .

#### 2.1.2 Reaction Sintering

In this method a physical mixture of a zinc compound is reacted with a titanium compound by rapid firing (less than 2 hr) at  $900^\circ\text{--}1500^\circ\text{C}$  to produce the pigment.

#### 2.1.3 Heat Treatment of Powders

Accelerated heat treatment of powders by flash heating (times of less than 5 min) or the rotary kiln concept.

### 2.2 Technical Discussions

#### 2.2.1 Laboratory Synthesis of Zinc Orthotitanate

A flow diagram for the present laboratory synthesis method for  $\text{Zn}_2\text{TiO}_4$  used at IITRI is shown in Figure 1. The process consists of a series of grinding and mixing operations, firing at  $925^\circ\text{C}$  for 18 hr, additional grinding, followed by reactive encapsulation and/or induction plasma calcining to obtain a stable

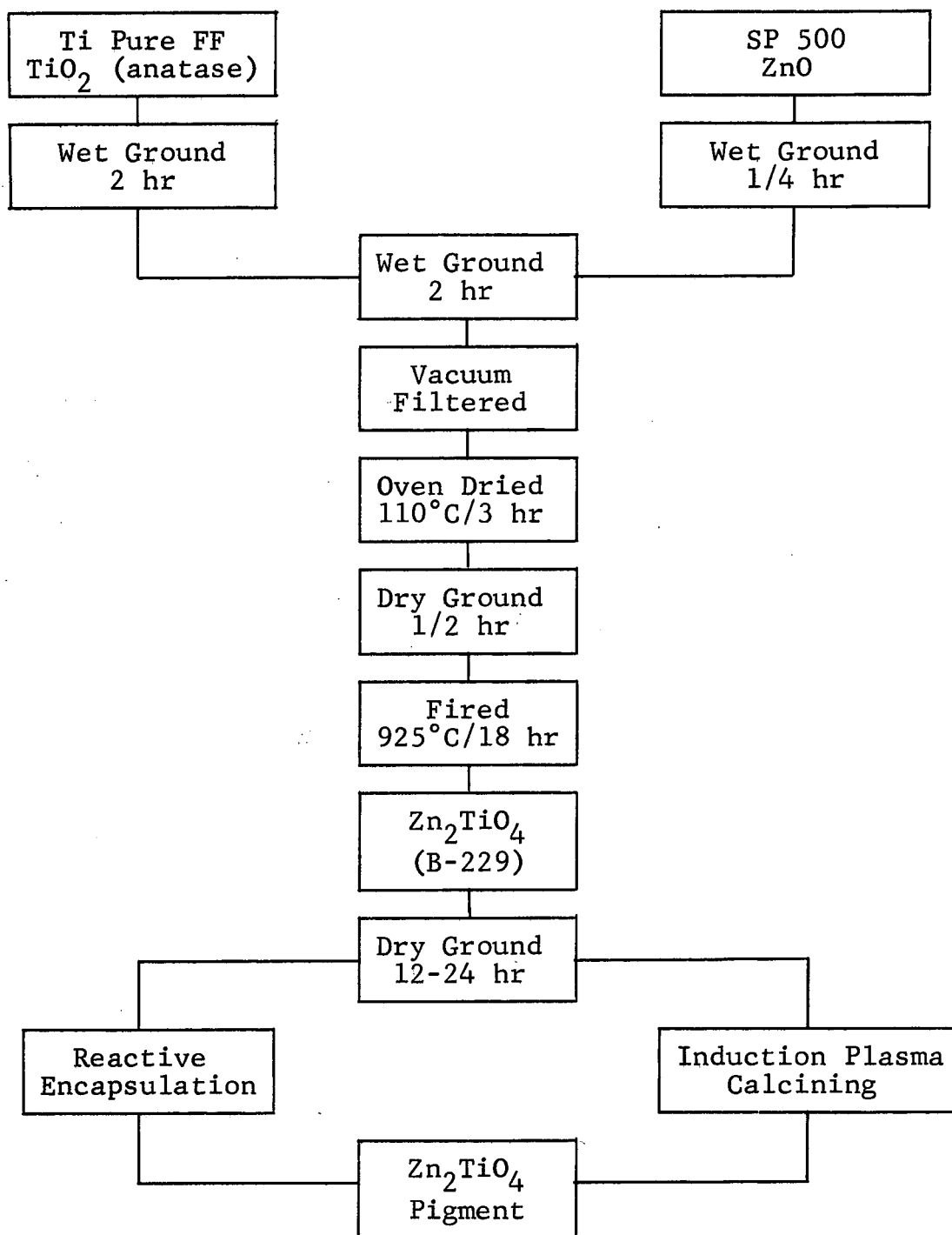


Figure 1 FLOW DIAGRAM FOR B-229 SYNTHESIS OF ZINC ORTHOTITANATE PIGMENT

product. A total of 4 hr of wet grinding and 1/2 hr of dry grinding is conducted prior to firing and this is followed by an additional 12-24 hr of grinding for comminution of the  $\text{Zn}_2\text{TiO}_4$  product.

Spectrographic analysis of a series of zinc orthotitanates prepared by this method revealed the following major oxide impurities in relative concentrations (Ref. 1):

<u>SRI Sample</u>	<u>Grind Time</u>	<u>Si</u>	<u>Al</u>
A-0	24 hr	0.5	0.3
B-0	24 hr	1.2	0.7
D-0	12 hr	0.1	0.25

These rather large amounts of Al and Si may be attributed to contamination from the porcelain grinding balls and would appear to be a function of grind time. Such impurities in a material can be a source of optical degradation in an ultraviolet radiation environment. Minimization of grinding times reduce contaminants and lessen the number of crystallographic defects.

Stabilization of zinc orthotitanate pigment subsequent to its synthesis at  $925^\circ\text{C}$  to prevent optical degradation is presently accomplished by either or both of the following methods: reactive encapsulation, induction plasma calcination. The latter method involves a rather sophisticated apparatus, and the yield is very low.

### 2.2.2 Basic Approach

Each of the three production methods exploits one or more of the mechanisms which increase the rates of reactions which in turn yield a reduction in synthesis times. Reaction time reductions limit agglomeration and grain growth, thus minimizing the need for comminution of particles.

Acceleration of the rate of reaction between two compounds can be accomplished by increasing temperature and/or pressure. The strong effect of temperature is shown by the Arrhenius equation:

$$\text{Log}_e K \text{ (reaction rate constant)} = S \cdot A \cdot \Delta H / RT = \text{constant} / T \quad (1)$$

The simultaneous use of pressure (as in hot pressing) to obtain particle-to-particle intimacy, and hence increased diffusion rates, produces higher reaction rates. Furthermore, the use of high surface area powders, which have increased activity, can be produced in a decomposition process, e.g.,

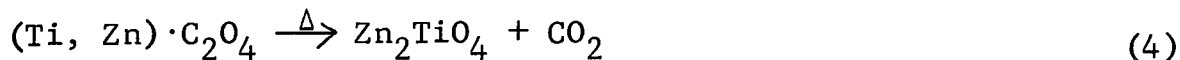
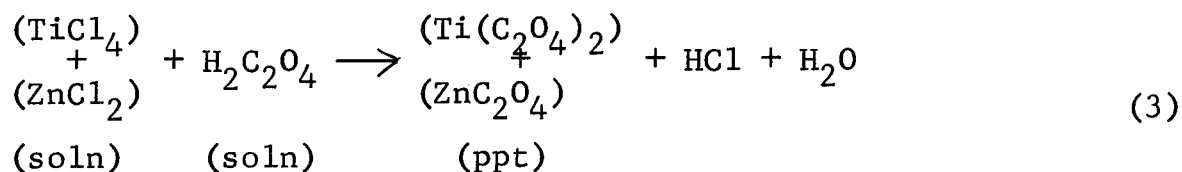


and the nascent surfaces of the ZnO thus obtained are highly reactive. Surface area effects as revealed in sintering studies of thorium oxide conducted at IITRI (Ref. 2) exemplify the advantage of using decomposable precursors for obtaining highly reactive products.

#### 2.2.2.1 Coprecipitation

The coprecipitation method involves the simultaneous addition of zinc and titanium chlorides to a solution of oxalic acid. The resulting solution is then heated to and held at a specified temperature, during which time it is continuously stirred. The precipitate is an intimate mixture of zinc and titanium oxalates. Because of its extremely fine particle size this mixture can be converted to  $\text{Zn}_2\text{TiO}_4$  at a relatively low temperature.

The method may be represented by the following generalized reactions:



The notation  $(\text{Ti, Zn}) \cdot \text{C}_2\text{O}_4$  is used to denote the mixed oxalate precipitate, the actual mole ratio of the respective oxalates being dependent upon many factors. Some of the more important

factors are the temperature of the oxalic acid solution, the solvent-alcohol or water, the holding time (time at temperature), and the method of chloride addition-dropwise or direct.

#### 2.2.2.2 Reaction Sintering

In this method of synthesis we utilize the reaction of a physical (as compared to a coprecipitated) mixture of a decomposable zinc compound with a titanium compound which also may be decomposable. The mixing of reactants in this method can be accomplished rapidly and with simplicity. An example of this method is the reaction at 600°C for 2 hr of TiH with the carbonate or oxalate of zinc. The reaction rate is slower in this method than in that of coprecipitation because of the intimately mixed, fine particle size mixture in the latter method. The advantages offered in this method include simple mixing of reactants, total heat treatment time (including heat-up and cool-down) as short as 1 hr, and higher yield.

#### 2.2.2.3 Heat Treatment of Powders

Our studies show that a stabilized  $\text{Zn}_2\text{TiO}_4$  is obtained by heat treatment of coprecipitated oxalates at 900°C. Additional stability may be gained for this material, or for that matter any  $\text{Zn}_2\text{TiO}_4$ , by still higher temperature heat treatments - up to 1500°C. In the heat treatment of precursor or  $\text{Zn}_2\text{TiO}_4$  pigment powders, however, excessive sintering must be avoided, since the agglomerates may be "clinkers" or otherwise ungrindable by normal means and/or they may be susceptible to contamination and introduction of defects through grinding.

Sintering of powder particles may be prevented or minimized by greatly reducing time at temperature or by eliminating particle-to-particle contact. Several concepts for achieving such heat treatment conditions have been considered, but not yet attempted experimentally. These include flash heating, rotary kiln, and fugitive matrix.

## 2.3 Laboratory Investigations

### 2.3.1 Coprecipitation

The initial step in the coprecipitation study is to optimize the technique for rapid mixing of reactants, and for obtaining reproducibility. The variables are the oxalic acid solvent (water or alcohol), solution pH, starting mixture (mol ratio of Zn:Ti), addition method (dropwise or direct dump), and reaction rates and conditions (temperature and holding time). The program plan is depicted in Figure 2. Gross composition of the precipitates are evaluated using x-ray techniques. Firing of these materials is conducted at 900°-1000°C for times of 2-10 hr, and the resulting powders are examined by x-ray diffraction to determine gross composition and crystal structure. The most important considerations for these titanate powders are the reflectance (or solar absorptance), and stability to solar ultraviolet radiation.

Although not necessarily ideal, the temperature and time conditions of calcination (900°C for 8 hr) were selected because previous studies had established that under such conditions a stable product is obtained (Ref. 3); and, of course, they were established in order to compare on an uniform basis products prepared under parametric conditions. Theoretically, the use of a 2:1 mole ratio of Zn to Ti in the mixed chloride solution should yield titanate of the desired stoichiometry, i.e.,  $\text{Zn}_2\text{TiO}_4$ . Previous experience has also shown (Ref. 3) that an excess of ZnO in the product is very much preferred to an excess of  $\text{TiO}_2$ , mainly because of the latter's insolubility and thus its unextractability. An initial objective of this work was thus to determine the effect of the Zn:Ti mol ratio on the composition of the final product. The effect of using water or methyl alcohol as the solvent for oxalic acid was also examined. To simplify and speed up this step in the processing, the mixed chlorides were added rapidly to the oxalic acid solution at room temperature. The systems were then heated to 90°C in the case of water, or to 55°C in the case of

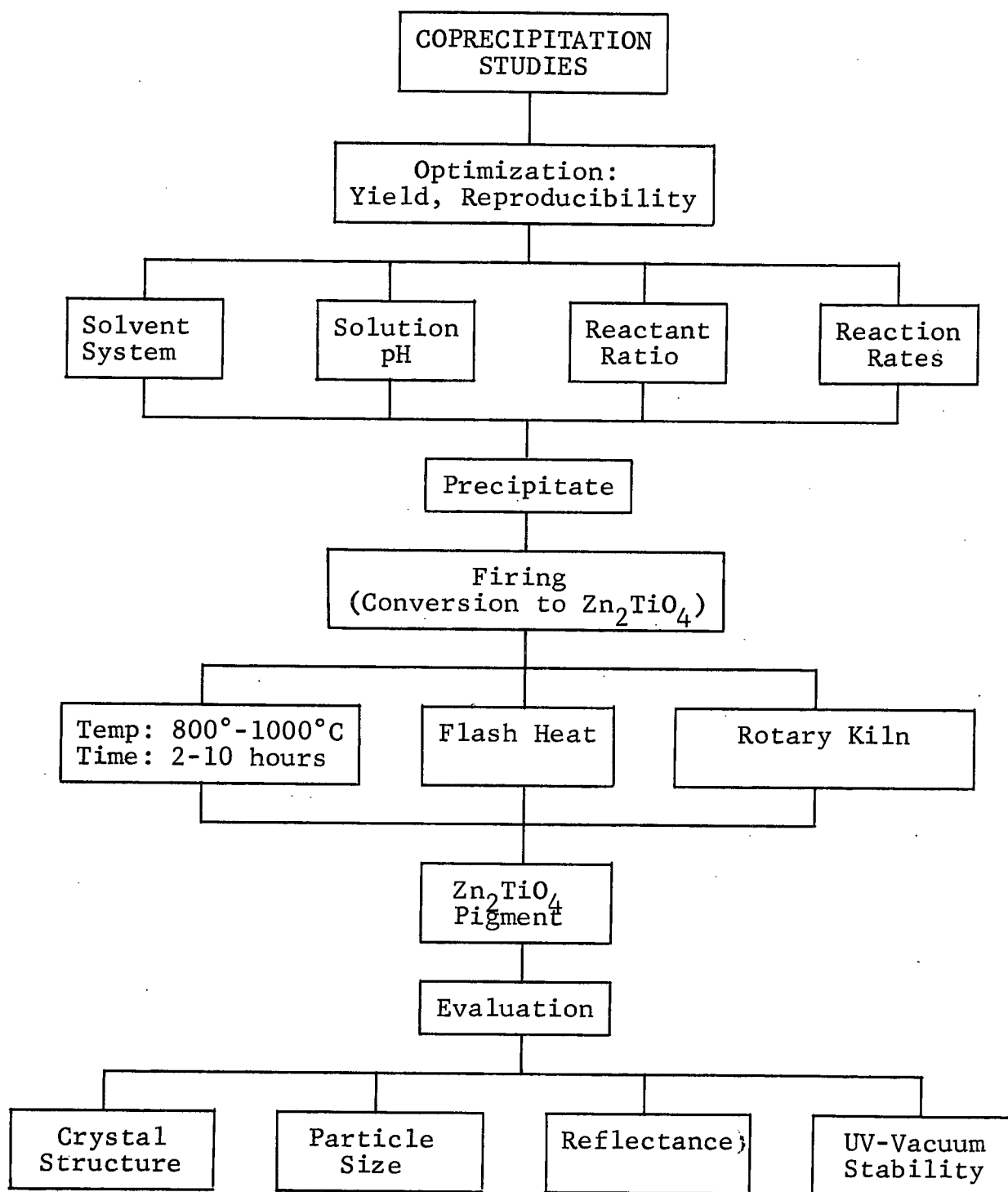


Figure 2 PROGRAM PLAN FOR COPRECIPITATION STUDIES



alcohol to complete the precipitation. After cooling, the solid product was obtained and heat treated at 900°C for 8 hr to obtain  $\text{Zn}_2\text{TiO}_4$ . The product appeared to be of a particle size small enough for direct use as a pigment, thus precluding the possibility of contaminant introduction in any grinding process that might be employed.

The data in Table 1 summarize the studies of coprecipitation. X-ray analysis shows that the precipitation product in the water system is two-phased, consisting of zinc oxalate and a second crystalline material which is designate as metatitanic acid ( $\text{H}_2\text{TiO}_3$ ). No standard x-ray pattern corresponding to the pattern of this second phase could be found in the literature. The designation as  $\text{H}_2\text{TiO}_3$  is based on information in the literature which reports this material as the hydrolysis product of a titanium salt in solution under prolonged heating (Ref. 4).

Analyses of fired products of water-based systems show that using a Zn:Ti mole ratio of 2:1 or higher results in zinc orthotitanate plus free zinc oxide. The 2:1 ratio (Zn:Ti) using a one hour hold during precipitation, followed by a 900°C/8 hr firing, produces a  $\text{Zn}_2\text{TiO}_4$  product which is a viable pigment.

In the alcohol systems, there was no evidence of  $\text{H}_2\text{TiO}_3$  in any of the precipitates. As shown in Table 1, the "co-oxalate" pattern was shown for the 2Zn:1Ti with a 5 min hold; all of the other precipitates gave x-ray patterns of zinc oxalate with no evidence of any crystalline titanium phase. However, all of the precipitates when fired at 900°C for 8 hr yielded free  $\text{TiO}_2$  or  $\text{Zn}_2\text{TiO}_4$ . Thus the titanium phase in the precipitate is either extremely fine or is in an amorphous state. For the alcohol system, a Zn:Ti mole ratio in excess of 2.5:1 but less than 3:1 is necessary to obtain  $\text{Zn}_2\text{TiO}_4$  with no  $\text{TiO}_2$  and a minimum of excess ZnO.

Single component precipitate studies have also been conducted, i.e., determining the precipitation product when either

Table 1

## EFFECT OF INITIAL Zn:Ti MOLE RATIO DURING COPRECIPITATION

Zn:Ti Mole Ratio In Mixed Chlorides	Solvent for Oxalic Acid	Precipitation		Precipitation Product	Fired Product 900°C/8 hr
		Temp. °C	Time, min.		
4:1	Water	90	5	$\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} + \text{"H}_2\text{TiO}_3\text{"}$ *	$\text{Zn}_2\text{TiO}_4 + \text{ZnO}$
2:1	Water	90	5	$\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} + \text{"H}_2\text{TiO}_3\text{"}$	$\text{Zn}_2\text{TiO}_4 + \text{ZnO}$
1.5:1	Water	90	5	$\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} + \text{"H}_2\text{TiO}_3\text{"}$	$\text{Zn}_2\text{TiO}_4 + \text{TiO}_2$
4:1	Methanol	55	5	$\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	$\text{Zn}_2\text{TiO}_4 + \text{ZnO}$
3:1	Methanol	55	5	$\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	$\text{Zn}_2\text{TiO}_4 + \text{ZnO}$
2:1	Methanol	55	5	"Co-oxalate"*	$\text{TiO}_2$
2:1	Water	90	60	$\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} + \text{"H}_2\text{TiO}_3\text{"}$	$\text{Zn}_2\text{TiO}_4 + \text{ZnO}$
2:1	Methanol	55	60	$\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	$\text{Zn}_2\text{TiO}_4 + \text{TiO}_2$

\*Standard x-ray patterns for " $\text{H}_2\text{TiO}_3$ " and "co-oxalate" could not be found in the literature. However, their patterns are reproducible and these designations will be used pending more definitive characterization.

$\text{TiCl}_4$  or  $\text{ZnCl}_2$  alone is reacted with oxalic acid. These experiments were for the purpose of identification of the precipitate using x-ray powder diffraction and also for the purpose of determining actual (vs theoretical) yield based on molecular weights.

The  $\text{ZnCl}_2$  reaction with oxalic acid rendered results straightforward to calculate, in that gravimetric analyses showed essentially a 100% yield for  $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  in the precipitate and for  $\text{ZnO}$  on calcination of  $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  at  $900^\circ\text{C}/8$  hr.

### 2.3.2 Flash Calcination Studies

Preliminary studies were conducted during this period in calcination of materials at  $1200^\circ\text{C}$  for 1 hr. Nine (9) coprecipitated materials were heat-treated in this manner. X-ray powder spectra show that the fired products at this temperature ( $1200^\circ\text{C}$ ) were essentially the same as those obtained from the same materials fired at  $900^\circ\text{C}/8$  hr, for most of the materials. However, three materials did show some changes as described below:

Sample	Phases Present After Heat Treatment at:	
	<u><math>900^\circ\text{C}/8</math> hr</u>	<u><math>1200^\circ\text{C}/1</math> hr</u>
LH-12	ZOT* + ZMT* + ZnO	ZOT*
LH-10	ZOT + ZMT = $\text{TiO}_2$	ZOT + $\text{TiO}_2$
LH-11	ZOT + ZMT + $\text{TiO}_2$	ZOT + $\text{TiO}_2$

\*ZOT = zinc orthotitanate, ZMT = zinc metatitanate

For all three samples, zinc metatitanate was not observed in the  $1200^\circ\text{C}$  calcined samples. This can be explained by examination of the  $\text{ZnO-TiO}_2$  phase diagram proposed by Dulin and Rase (Ref. 5) in which dissociation of  $\text{ZnTiO}_3$  to  $\text{Zn}_2\text{TiO}_4$  plus  $\text{TiO}_2$  at  $945^\circ\text{C}$  is indicated. A significant point is that in LH-12, both ZMT and ZnO were present in the  $900^\circ\text{C}$  material. A higher heat treatment of  $1200^\circ\text{C}$  resulted in a material which revealed only ZOT lines, indicating reaction between the excess ZMT and ZnO to form ZOT.

### 2.3.2.1 Pigment Stability Considerations

The latter observations may be highly important in that the ultraviolet instability of  $\text{Zn}_2\text{TiO}_4$  pigments has not been directly correlated with their stoichiometry or particle (or crystallite) size. The general expectation is that the higher temperatures would produce a more ordered crystalline system and a larger particle size. This latter system would be expected to be more stable for the reasons that stoichiometric defect possibilities are less and that there is less "surface." Because of the latter consideration, particle size becomes very important. The ultraviolet radiation penetration zone, as a fraction of total particle volume, decreases very significantly as particle size increases. The processes that increase particle size also produce higher internal order. The question then becomes: what is the optimum particle size for  $\text{Zn}_2\text{TiO}_4$  stability and - most importantly - what are the parameters and their values which lead to producing a stable material of optimum particle size.

### 2.4 Conclusions

From our analyses of experiments we have determined the Zn:Ti mole ratios necessary for obtaining a pure  $\text{Zn}_2\text{TiO}_4$  free of excess  $\text{TiO}_2$  and  $\text{ZnO}$ . Significantly, the rapid direct mixing technique as opposed to the slow dropwise technique, can be used to produce  $\text{Zn}_2\text{TiO}_4$ , facilitating the scale-up of the process. Since the fired product of the flash calcination also appears to be in the form of fine particles, comminution may not be necessary.

Tentatively, then, the selected starting composition involves a Zn:Ti mole ratio of 2:1 added as a mixed chloride solution to a water solution of oxalic acid. This produces a mixed oxalate precipitate with a yield of 91% of theoretical. The composition of this co-precipitate is  $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  plus  $\text{TiOC}_2\text{O}_4$ . The mole ratio of the two materials is as planned, slightly in excess of 2 Zn to 1 Ti.

Two production methods (one in water and one in alcohol) for obtaining sizable quantities of  $\text{Zn}_2\text{TiO}_4$  are feasible. Several refinements, however, may yet be made to obtain a more stable product with the desired optical characteristics, e.g., removal of excess  $\text{ZnO}$  with acetic acid, and/or flash firing at higher temperatures.

Even though the dropwise coprecipitation method is slower, the fact that it leads to a stable product (after a  $900^\circ\text{C}/8$  hr firing) makes it a valuable back-up to the direct addition method. In either case scaling up the process to yield pound and more quantities should not be difficult.

### 3. OWENS-ILLINOIS 650 GLASS RESIN IMPROVEMENT

#### 3.1 Background

The unsuitability of Owens-Illinois 650 (OI-650) Glass Resin as a paint vehicle has been documented previously (Ref.'s 3 and 6). For the sake of completeness, however, we will briefly state the problem and the general nature of the approach to solving it. The incentive for improving it, of course, is its exceptional optical stability under ultraviolet irradiation in vacuum.

Owens-Illinois 650 cures by thermally induced cross-linking at hydroxyl sites. Because it is prepared from a wholly tri-functional silane, OI-650, upon curing, tends to form three dimensional bridges - a "stereo" ladder structure. As a result a film cast from this material becomes hard and brittle, and continues to cure with time (to "coast") by reaction of the residual hydroxyl groups, however small in number. The coasting increases the hardness and the internal strain to the point that, in highly pigmented systems, cracking and crazing results. The general approach to preventing coasting is to introduce into the polymer structure groups that provide internal plasticization, or inhibit the curing process, or end-block the polymer (limiting its ultimate molecular weight). The added material, of course, must not affect the environmental stability of the basic resin. Of the various methods attempted, end-blocking has been by far the most successful.

#### 3.2 Synthesis

For the reasons discussed in the previous triannual report (Ref. 6), dimethyl formamide (DMF) was employed as the reaction medium. The procedure utilized for the synthesis of end-blocked polymers was the following:

Owens-Illinois 650 resin (25g) was dissolved in DMF (75cc). Trimethylchlorosilane (TMCS) was added from a buret while the solution was vigorously stirred and cooled with ice. When the addition was completed, the reaction was permitted to continue

overnight at room temperature. The polymer precipitate was isolated, washed once with DMF and three times with methanol, and then dried in a vacuum oven for 24 hr at 94°F.

This general procedure was employed with various ratios of TMCS/OI-650 (0.2 - 0.5cc TMCS/g OI-650). A soluble resin was obtained by using a concentration of TMCS equivalent to 0.44cc/g OI-650 or higher. At lower levels of TMCS, insoluble products (gels) were obtained.

Several samples, prepared by using 0.44cc TMCS/g OI-650, were evaluated as coating materials. One such sample gelled during drying, when the temperature of the oven was increased from 94°F to 100°F. The drying temperature therefore must be carefully controlled.

### 3.3 Engineering Evaluations

Two samples of the modified OI-650 resin, designated OI-650G, were submitted to the paint laboratory for preliminary evaluations, each sample being approximately 23 grams. The resin (at 100% solids) was colorless, transparent, plastic, viscous, and extremely tacky.

Extensive solubility tests were conducted, the results of which are summarized in Table 2. Solubility was determined by visual observations. The procedure involved the following steps: the resin was dispersed in the test solvent and its solution properties noted; and the films cast from these solutions were then checked for appearance and physical properties. The symbols in Table 2 are identified in the key. In general the hydrocarbons are the best solvents for OI-650G.

Two different thinner formulae were used and evaluated for making a 50% solution of the resin

#### "Mix α"

Benzene	75% by volume
Isopropyl Acetate	15%
Isopropyl Alcohol	10%

Table 2

## LIST OF SOLVENTS

<u>Hydrocarbons</u>	<u>Solution</u>	<u>Film</u>
Petroleum ether	±*	±*
Benzene	+	+
Toluene	+	+
Xylene	+	+
Ethyl benzene	+	±
<u>Alcohols</u>		
Methyl alcohol	p	i
190p Ethyl Alcohol	p	i
200p Ethyl Alcohol	±	±
150p Isopropyl Alcohol	±	+
Butyl Alcohol	+	+
Methyl Isobutyl Carbinol	+	+
<u>Esters</u>		
Ethyl Acetate	±	±
180p Isopropyl Acetate	+	+
n-Butyl Acetate	+	+
Methyl Amyl Acetate	+	+
Cellosolve Acetate	+	+
		(poor solvent release)
<u>Ketones</u>		
Acetone	±	±
Methyl-ethyl Ketone	±	±
Methyl Isobutyl Ketone	+	+
Diacetone	p	p
Cyclohexanone	p	p
<u>Cellosolves</u>		
Methyl Cellosolve	p	p
Ethyl Cellosolve	p	p
Butyl Cellosolve	p	p
<u>Nitro Compounds</u>		
2-Nitropropane	p	p

\*Key: + = soluble clear  
 ± = soluble hazy  
 i = insoluble  
 p = precipitate forms



	<u>"Mix <math>\beta</math>"</u>
Toluene	75% by volume
Butyl Acetate	15%
Butanol	10%

Pours of each solution were made over tin strips, one of which was air-cured overnight, the other cured at 212°F overnight. On pouring acetone across the cured pours the following day, the air cured pours were badly eroded, while the baked pours were not eroded but did show a white "bloom" where the acetone had been poured. This suggests very little cross-linking from an air cure and an incomplete cure with the 212°F bake. The air cured pours were much more tacky than the backed ones, and the "mix  $\alpha$ " pours were tackier than the "mix  $\beta$ " pours. This latter finding shows that the use of a slower (less volatile) solvent kept the coating open longer for a better final dry.

Using "mix  $\beta$ ", two grinds were made of zinc orthotitanate pigment (lithium silico fluoride treated and flash re-calcined), one at 26% Pigment Volume Concentration (PVC) and the other at 35% PVC. Both grinds were sprayed on clean aluminum and the panels baked overnight at 212°F. The 26% PVC coating, while not tacky to the touch, exhibited some evidence of dirt collection under warm pressure particularly when making conical mandrel and 10-inch pound reverse impact tests. The 35% PVC coating gave better results. Both panels passed the conical mandrel and 10 in-pound reverse impact tests.

It was determined that baking for 16 hr at 212°F is required to provide a coating not readily soluble in the original solvent. Paints, pigmented at 35% PVC with S-13G pigment (potassium silicated SP500 ZnO), possess shelf-lives of at least 2 months; none have gelled yet. (It should be noted that unmodified OI-650 resin cannot usefully be pigmented with silicated zinc oxide, the mixture gels almost instantly.) A series of paint films employing S-13G and zinc orthotitanate pigments were prepared in order to

establish the cure conditions. One series, designated A-429M, was S-13G pigment in OI-650G; one, zinc orthotitanate in OI-650, and one in OI-650G. Out of each series, one film was air dried, one was cured at 250°F/16 hr, and a third cured at 350°F/16 hr. All of the unmodified films showed evidence of cracking, while the OI-650G films did not. The modified films definitely require an heat cure. Although 250°F produces a satisfactory cure, the 350°F treatment is preferable. All of the films which were heat cured displayed excellent adhesion and film toughness. Their general appearance was also very good.

### 3.4 Conclusions

From these tests, other visual observations and from comparisons, it is clear that OI-650G paint films do not crack or lose adhesion as do those using unmodified OI-650. The PVC is best kept above 32%; a PVC of 36% has been standardized in the laboratory. Curing should be accomplished at 250°F preferably 350°F, at least overnight. The recommended solvent is F26, a mixture of toluene (75%), butyl acetate (15%) and butanol (10%). The overall experimental results indicate that the coating problem has been solved without any sacrifice in optical performance. The stability data presented in Section 6 speaks for itself.

#### 4. FORMULATION OF A-429M

##### 4.1 Introduction

The formulation of A-429, the precursor to A-429M, was first reported in early 1969 in a report to the Jet Propulsion Laboratory on the development of S-13G as an engineering material (Ref. 6). This work was subsequently published in the open literature (Ref. 7) and later summarized in the final report on NASA Contract NAS8-5379 (Ref. 3). Coating A-429 is an Owens-Illinois 650 resin paint pigmented with potassium silicate treated zinc oxide. This paint was made practical by the sodium acid phosphate-washing step described in these reports. This additional step was added to the S-13G-pigment manufacturing process (a step that is now part of the standard S-13G process) in order to preclude the instant gelling that occurred when the too-alkaline precursor pigment was added to the Owens-Illinois 650 resin. The phosphating step allowed for sufficient shelf life to make experimental paints--but the shelf life was still not long enough for practical spacecraft applications. Additionally, the previously mentioned "coasting" problem exhibited by Owens-Illinois 650 resin would have precluded employment of such a pigmented coating anyway. (It should be noted, however, that, although "coasting" is a major problem with all non-catalyzed, 100%-methyl silicone resins, it is not a serious problem for unpigmented Owens-Illinois 650 resin coatings provided they are properly applied.)

##### 4.2 A-429M

It was the successful end-blocking of Owens-Illinois 650 resin (described in the preceding section) that permitted the reformulation of potassium silicate treated ZnO in A-429, now designated A-429M. It was expected that this coating would not exhibit "coasting," would require baking to optimize cure, would be adherant and would be resistant to wide temperature variations (including LN<sub>2</sub> thermal shock), would possess exceptional optical stability (equal to A-429), and would have adequate shelf-life as

a result of the end-blocking of residual functionality of the polymer (thus precluding alkaline-pigment-catalyzed gellation). The modified 650 resin (GA-30) was diluted with 180 parts of solvent T-26 and changed to a porcelain ball mill. The pigment was added, premixed and ground for 2 hr. The PVC (pigment volume concentration) was 36% and the viscosity was 14 sec Ford Cup No. 4. The shelf life exceeds 60 days. The formulation of the A-429M samples tested for ultraviolet stability is shown in Table 3.

Table 3

FORMULATION OF A-429M THERMAL-CONTROL PAINT  
(Batch C-406)

Silicated ZnO (Batch C-390)	360 pbw*
Owens-Illinois 650G (Batch GA-30)	180 pbw
Solvent T-26	360 pbw
<u>T-26</u>	
Toluene	75% w/o
n-Butyl Acetate	15% w/o
n-Butyl Alcohol	10% w/o

\*parts by weight

#### 4.3 Evaluation

Specimens of Batch C-406 of A-429M were prepared using the three different curing schedules shown in Table 4. Where the physical properties of the resultant coatings are also noted.

Table 4

A-429 COATINGS-EFFECTS OF CURE SCHEDULE

Coating No. and Cure	Physical Properties
(A) 24 hr room temperature	Printable, glossy coating
(B) 16 hr at 250°F	Moderately-hard, semi-glossy enamel
(C) 16 hr at 250°F plus 2 hr at 350°F	Hard, dead-flat enamel

IRIF coupons of the baked coatings were irradiated in both IRIF-I (1500 ESH at 150°F for both (B) and (C)) and in the CREF (IRIF-II) (3000 ESH at 50°F for (B)). The exceptional stability exhibited by A-429M in all three cases is discussed in a later section of this report.

## 5. ELECTRON PARAMAGNETIC RESONANCE INVESTIGATIONS

### 5.1 Introduction

Most of the research work centered around the investigation of the iron resonance in  $\text{Zn}_2\text{TiO}_4$ , and the preliminary characterization of  $\text{Zn}_2\text{TiO}_4$  pigments prepared by the coprecipitation process. The suggestion had been made that the iron might in fact be a contaminant, either present in the starting materials ( $\text{ZnO}$  and  $\text{TiO}_2$ ), or introduced in our manufacturing process. This question has been partially resolved and a possible source of contamination tentatively identified.

Research also involved the characterization of pigments produced by the coprecipitation process. Two pigments have been partially investigated to date; some basic differences have been noted and are reported.

### 5.2 Iron Resonance Investigations

#### 5.2.1 Sample Descriptions

Table 5 contains a summary of the samples investigated in an attempt to characterize the origin of the iron resonance in zinc orthotitanate at  $g = 4.25$ .

Table 5

#### IRON RESONANCE SAMPLES

<u>Sample</u>	<u>Description</u>
$\text{ZnO}$	N.J. Zinc SP500
$\text{TiO}_2$	DuPont FF Anatase
$\text{TiO}_2$	DuPont FF Anatase converted to rutile by heating
$\text{Zn}_2\text{TiO}_4$	IITRI Batch B-229 (prepared in stainless steel vessels)
$\text{Zn}_2\text{TiO}_4$	IITRI Batch C-405 (prepared in glass vessels)
$\text{Zn}_2\text{TiO}_4$	IITRI Batch C6233/4 (prepared by coprecipitation)
$\text{Zn}_2\text{TiO}_4$	IITRI Batch C6233/4 reheated at $900^\circ\text{C}$ for 5 hours

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As implied in Table 5, both starting materials ( $\text{ZnO}$  and  $\text{TiO}_2$ ) and the resultant pigments ( $\text{Zn}_2\text{TiO}_4$ ) were investigated in an attempt to pinpoint sources of iron contamination in the pigments.

### 5.2.2 Results

In Table 6 we summarize the results of the iron investigation. Typical spectra of the iron resonance at  $g = 4.25$  were presented and thoroughly discussed in Reference 6.

Table 6  
RESULTS OF IRON INVESTIGATION

Sample	Result
ZnO	No iron found
$\text{TiO}_2$ (anatase)	No iron found
$\text{TiO}_2$ (rutile)*	Iron present
$\text{Zn}_2\text{TiO}_4$ (IITRI <sup>4</sup> Batch No. B-229)	Iron present
$\text{Zn}_2\text{TiO}_4$ (IITRI <sup>4</sup> Batch No. C-405)	Iron present
$\text{Zn}_2\text{TiO}_4$ (IITRI <sup>4</sup> Batch No. C6233/4)	No iron found
$\text{Zn}_2\text{TiO}_4$ (IITRI <sup>4</sup> Batch No. C6233/4)	No iron found

\*FF anatase converted to rutile

### 5.2.3 Discussion

With respect to possible sources of iron, consider the results presented for the first six samples in Table 6. No iron was found in the  $\text{ZnO}$  or  $\text{TiO}_2$  as either comes from the manufacturer. Also, no iron was found in the pigment produced by the coprecipitation method. Only those samples prepared by high temperature solid-solid reaction (B-229) method contained iron. Even a sample which was prepared by this latter method but kept scrupulously free of iron showed an iron resonance. The key was provided by the sample of  $\text{TiO}_2$  (rutile) which was made by heating FF anatase. The only difference between the precursor and resultant  $\text{TiO}_2$  was the

conversion (heating) process. Two possible sources for iron in this process could be either the heating elements or the ceramic containers. Which of these possible sources is responsible for the iron contamination has not yet been determined.

### 5.3 EPR Characterization of Coprecipitation Method $\text{Zn}_2\text{TiO}_4$ Pigments

#### 5.3.1 Sample Descriptions

Two samples of  $\text{Zn}_2\text{TiO}_4$  prepared by the coprecipitation method have been briefly investigated. Sample C6233/4 according to x-ray powder patterns, contained an excess of  $\text{ZnO}$ . A second sample, No. C6233/13, contained excess  $\text{TiO}_2$ .

Only small amounts of each of these samples were available for EPR investigation. This fact, coupled with a loss of instrument sensitivity (described later in this section) prevented direct comparisons of spectra from the irradiated and unirradiated states of the pigment C6233/4.

#### 5.3.2 Results

Sample C6233/4 was placed in a quartz EPR tube and evacuated to  $10^{-7}$  torr using a previously described pumping system (Ref. 6). The EPR spectrum of the unirradiated pigment was recorded, but no resonances were observed. The sample was then irradiated at room temperature for 2 hr and for another 5 hr using the ultraviolet radiation from an Osram 500 watt point source lamp. Again, after both periods no resonances were observed. Subsequent observation of a standard sample indicated a malfunctioning of the EPR spectrometer which was traced to a bent arm on the "magic Tee" of the x-band bridge. This replaced. Since nearly all of the available C6233/4 had been irradiated, a correlation of the spectrum of pigment in its unirradiated state with that in its irradiated state was not possible.

Sample C6233/4 has also been air bleached and heated in air at  $900^\circ\text{C}$  for 5 hr in an attempt to bleach or destroy the resonances present.



A spectrum of C6233/4 appears in Figure 3. The EPR spectrum was obtained at 77°K in a vacuum of  $10^{-7}$  torr. The narrow symmetric resonance at  $g = 1.9561$  is identified as the ultraviolet sensitive resonance in ZnO discussed in Reference 6. The broad resonance, approximately 60 G wide, at  $g_{11} = 2.101$  and  $g_1 = 2.056$  has never been observed in any of the previous pigments investigated. An attempt to identify this resonance is in progress. A second, less intense and somewhat narrow resonance seems to be overlapping the broad resonance.

An attempt was made to air bleach the resonances observed, no changes in the resonances occurred. An attempt to anneal the resonances by heating at 900°C for 5 hr also proved ineffectual. Only the EPR spectrum of unirradiated C6233/13 has been observed to date. No resonances could be detected.

The uncertainty in the characterization of the unirradiated state of C6233/4 makes it uncertain whether the broad signal at  $g_{11} = 2.101$  and  $g_1 = 2.056$  was created by ultraviolet irradiation or is intrinsic to the sample. However, since air bleaching and heating in air at 900°C for 5 hr had no effect on this resonance, its response to these treatments is unlike any other ultraviolet-created resonance that has been investigated previously.

Heating C6233/4 at 900°C produced no resonance at  $g = 1.956$ . Although this resonance has always been observed in pigments with excess ZnO fired at these temperatures, its existence in pigments prepared by this method is not assured, mainly because of the different starting materials in this method.

The fact that no resonances were observed in the unirradiated state of C6233/13 implies that the stoichiometry of the starting materials in the coprecipitation process may be as important in determining the structure and contaminants of the final product as it is in the solid state reaction.

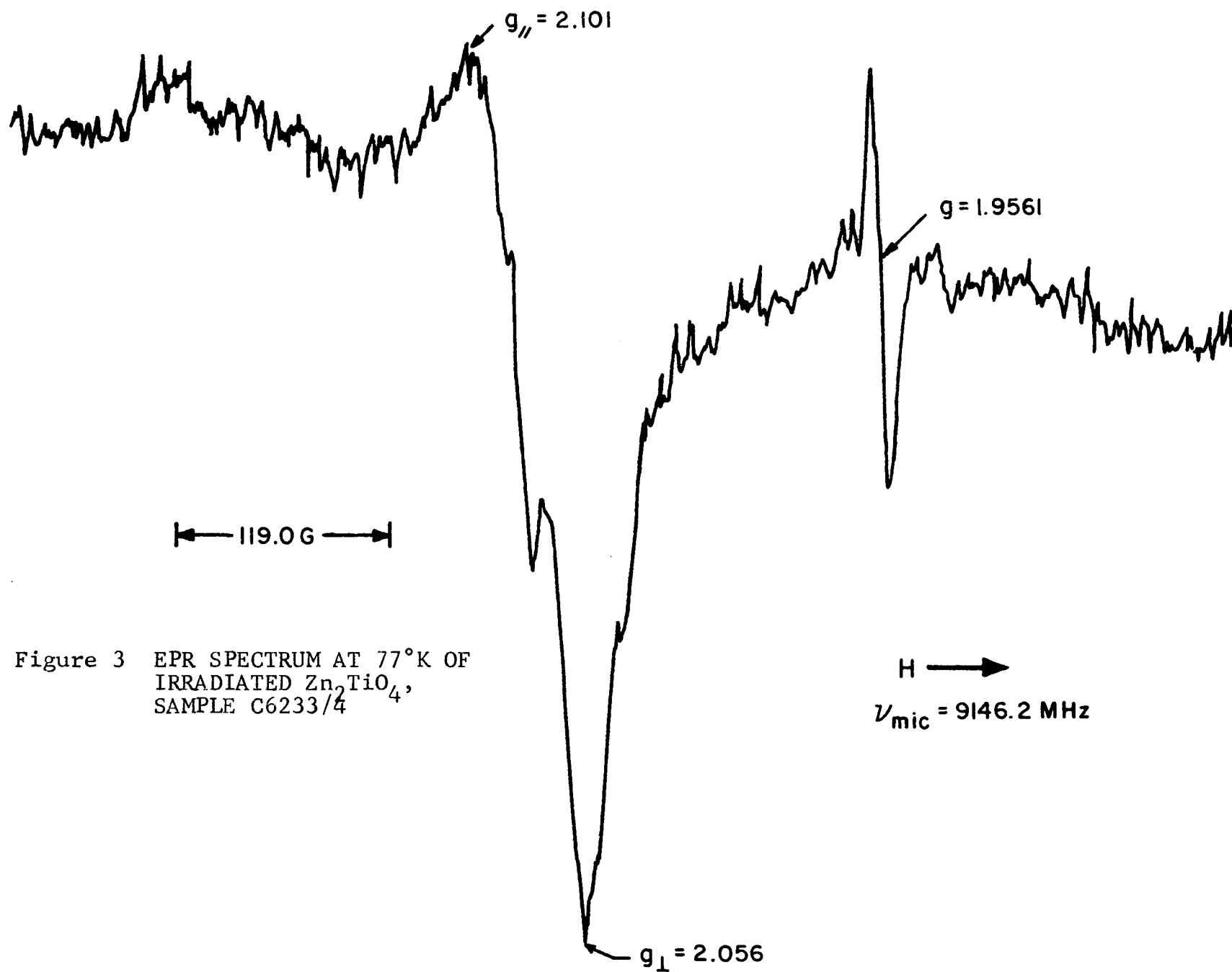


Figure 3 EPR SPECTRUM AT  $77^{\circ}\text{K}$  OF  
IRRADIATED  $\text{Zn}_2\text{TiO}_4$ ,  
SAMPLE C6233/4

#### 5.4 Zinc Orthotitanate Silicone Interactions

In previous work (Ref. 3), EPR investigations demonstrated that, when OI-650 and other silicone resins were ultraviolet irradiated, as many as four different free radicals were produced which are stable at  $\approx 77^\circ\text{K}$ ; but they disappear at room temperature. Also, it was shown that when a paint consisting of  $\text{Zn}_2\text{TiO}_4$  and OI-650 silicone resin is ultraviolet-irradiated, no free radicals of the type seen in the unpigmented silicone resins are observed.

Although the experiments and analyses are not complete, a preliminary explanation is that the free radicals are indeed formed but give up their electrons to the pigment molecules. We believe that the interaction of these electrons with the  $\text{Zn}_2\text{TiO}_4$  surface results in the formation of strong damage spectra centered at about 900 nm. Further, the interactions are precluded by ensuring that the pigment is either inherently stable itself or encapsulated in a protective layer.

#### 5.5 Conclusions

Since some experiments, as outlined above, remain to be completed, no concrete conclusions regarding the work to date can be made. However, the results so far indicate that the iron resonance previously observed may have been introduced as a contaminant during the pigment manufacturing process. If this is the case, process changes can be effected to eliminate iron contamination.

It is too early to form any conclusions regarding the performance of the coprecipitation pigments as compared with that of other pigments. This is especially true in view of the difficult nature of the surface protection/encapsulation problem in OI-650.

## 6. IRRADIATION TESTS AND RESULTS

Three irradiation tests have been completed during the reporting period. The results of each will be discussed in detail. Emphasis has been placed on the development and evaluation of zinc orthotitanate as a pigment and on OI-650G - an IITRI modification of the basic Owens-Illinois 650 glass resin. Most importantly, we have tested and evaluated a new paint system, designated A-429M, which, as will be indicated later, possesses superior optical stability.

### 6.1 CREF Test No. 8

#### 6.1.1 Background

CREF Test No. 8 was conducted at a simulated solar intensity of four (4) equivalent suns. Spectral reflectance measurements were made prior to irradiation, after 396 ESH (Equivalent Sun Hours) and  $5.5 \times 10^{14} \text{ p}^+/\text{cm}^2$ , after an additional 1032 ESH, and finally after an  $\text{O}_2$  bleach.

Except for Sample No. 12, all of the samples are zinc orthotitanate/OI-650 paints. Sample No. 5 is a paint which was supplied to the Air Force Material Laboratories for incorporation in an Air Force satellite flight experiment. Table 7 lists the paints, their pre-treatments, and  $\alpha_s$  values before and after irradiation.

#### 6.1.2 Test Results

The effects of ultraviolet exposures of nominally 400 ESH (plus  $5.5 \times 10^{14} \text{ p}^+/\text{cm}^2$  in the case of samples 1-4) and of an additional 600 ESH can be seen in the reflectance spectra in Figures 4-15. The appropriate solar absorptance values are provided in Table 7. Figure 4 shows the reflectance spectra of Sample No. 12, a heat treated zinc oxide powder. This material was included in the test as an indicator of ultraviolet damage. It's spectral reflectance loss is highly characteristic and within nominal degradation limits. Figures 5-8 are reflectance spectra of a paint whose pigment has been encapsulated in acid phosphate, treated with potassium silicate, and subsequently neutralized with acid phosphate. Samples 1 and 2 (Figures 5 and 7) were exposed

Table 7

## CREF ZINC ORTHOTITANATE PAINT\* SAMPLES AND TREATMENTS

Sample (Position) Number	Treatment/Vehicle	Paint Batch No.	Figure Number	Solar Absorptance Values			
				Initial	400 ESH**	1000 ESH	O <sub>2</sub> Bleach
1	:(PO <sub>4</sub> /SiO <sub>3</sub> /PO <sub>4</sub> )/OI-650	C-384	5	.134	.218	.225	.179
2	:(PO <sub>4</sub> /SiO <sub>3</sub> /PO <sub>4</sub> )(heat treated)/OI-650	C-379	7	.214	.342	.399	.332
3	:K <sub>2</sub> SiF <sub>6</sub> (re-heat treated)/OI-650	C-378	9	.245	.299	.346	.310
4	:K <sub>2</sub> SiF <sub>6</sub> /OI-650	C-383	11	.171	.216	.228	.197
5	:K <sub>2</sub> SiF <sub>6</sub> (re-heat treated)/OI-650	C-317	13 (AFML Flt. Exp.)	.152	.189	.194	--
6	:(PO <sub>4</sub> /SiO <sub>3</sub> /PO <sub>4</sub> )/OI-650	C-384	6	.154	.170	.191	.157
7	:(PO <sub>4</sub> /SiO <sub>3</sub> /PO <sub>4</sub> )(heat treated)/OI-650	C-379	8	.242	.357	.393	.325
8	:K <sub>2</sub> SiF <sub>6</sub> (re-heat treated)/OI-650	C-378	10	.244	.324	.332	.284
9	:K <sub>2</sub> SiF <sub>6</sub> /OI-650	C-383	12	.143	.203	.225	.184
10	:Li <sub>2</sub> SiF <sub>6</sub> /OI-650	C-382	14	.143	.162	.202	--
11	:Li <sub>2</sub> SiF <sub>6</sub> (heat treated)/OI-650	C-377	15	.175	.240	.256	--
12	Heat treated SP500 ZnO	--	4	.169	.178	.198	--

\*All the raw zinc orthotitanate was from IITRI Batch No. C-316, except Sample No. 5 which came from IITRI Batch No. B-492.

\*\*Samples 1-4 also received  $5.5 \times 10^{14} \text{p}^+(1.2 \text{ keV})/\text{cm}^2$ .

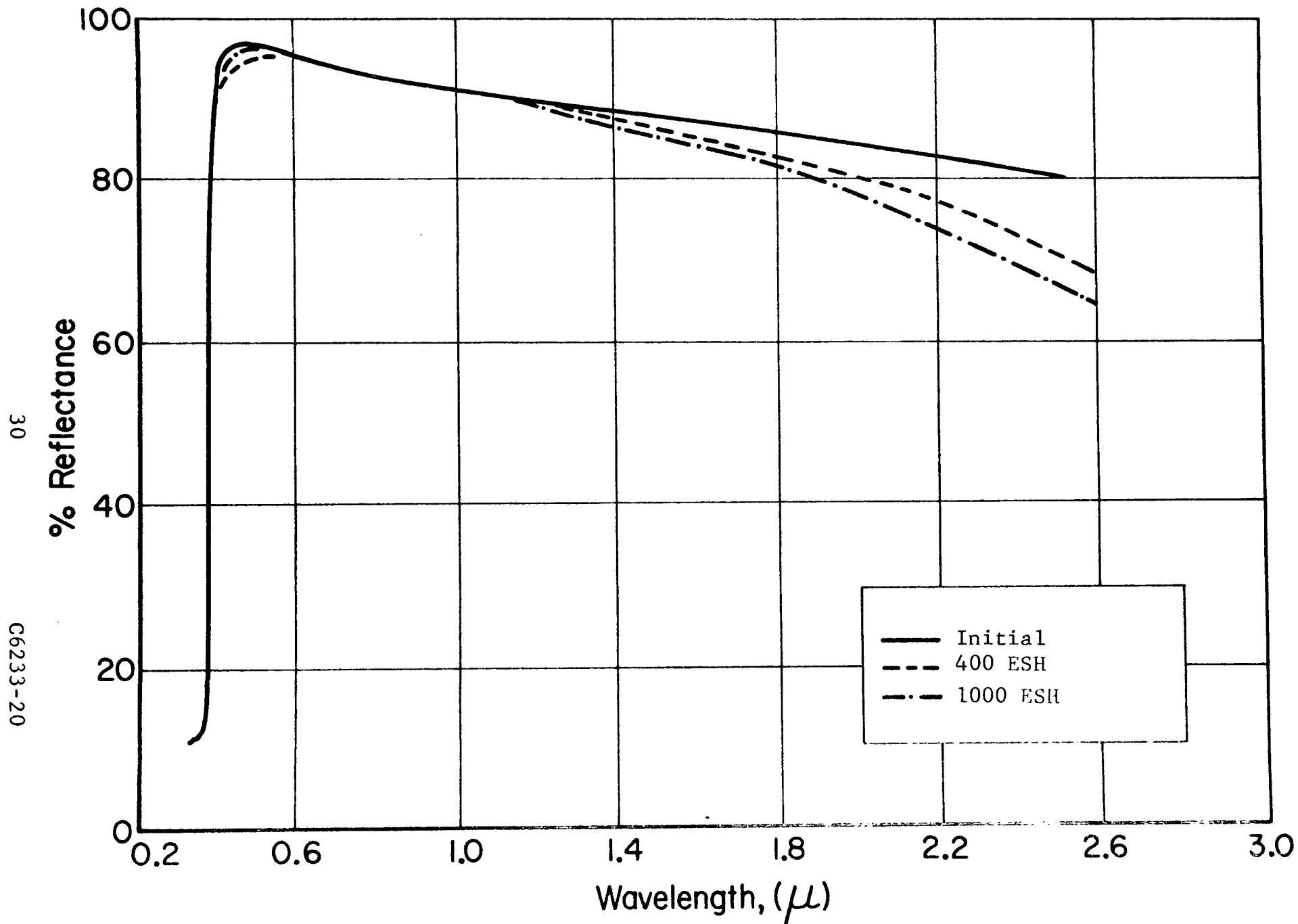


Figure 4 SPECTRAL REFLECTANCE OF HEAT TREATED SP-500 ZnO

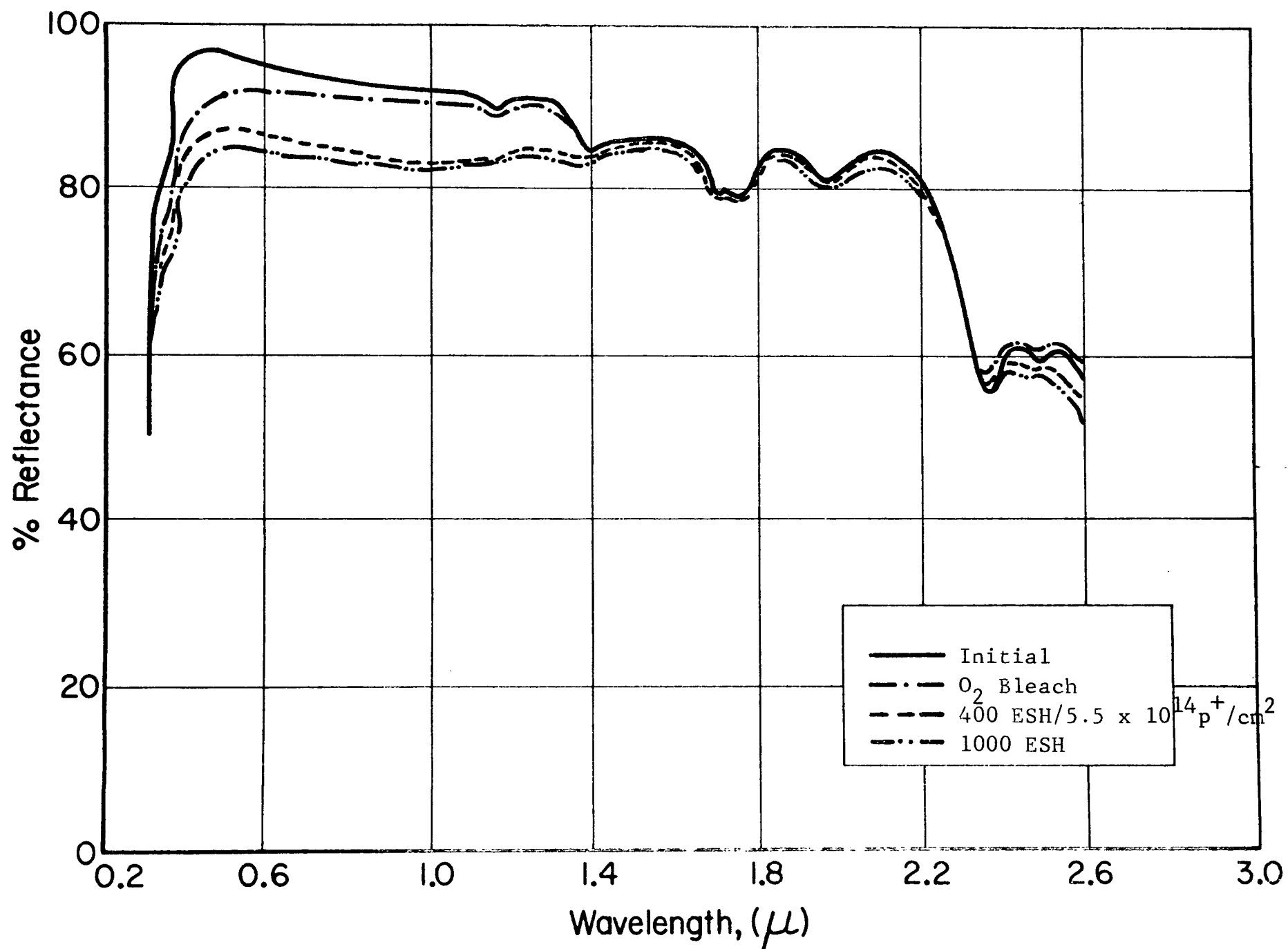


Figure 5 SPECTRAL REFLECTANCE OF  $Zn_2TiO_4:(PO_4/SiO_3/PO_4)/OI-650$

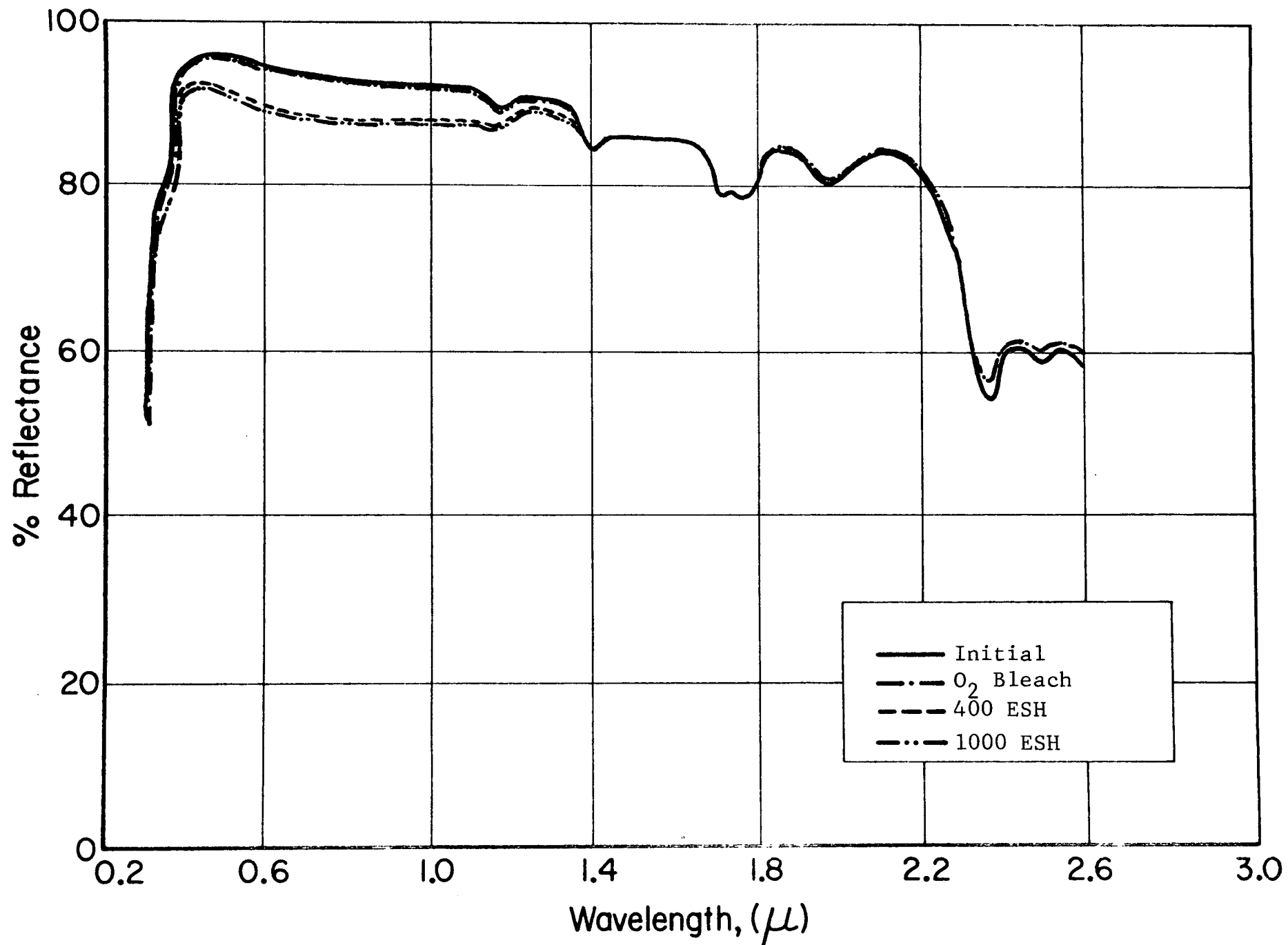


Figure 6 SPECTRAL REFLECTANCE OF  $\text{Zn}_2\text{TiO}_4:(\text{PO}_4/\text{SiO}_3/\text{PO}_4)/\text{OI-650}$



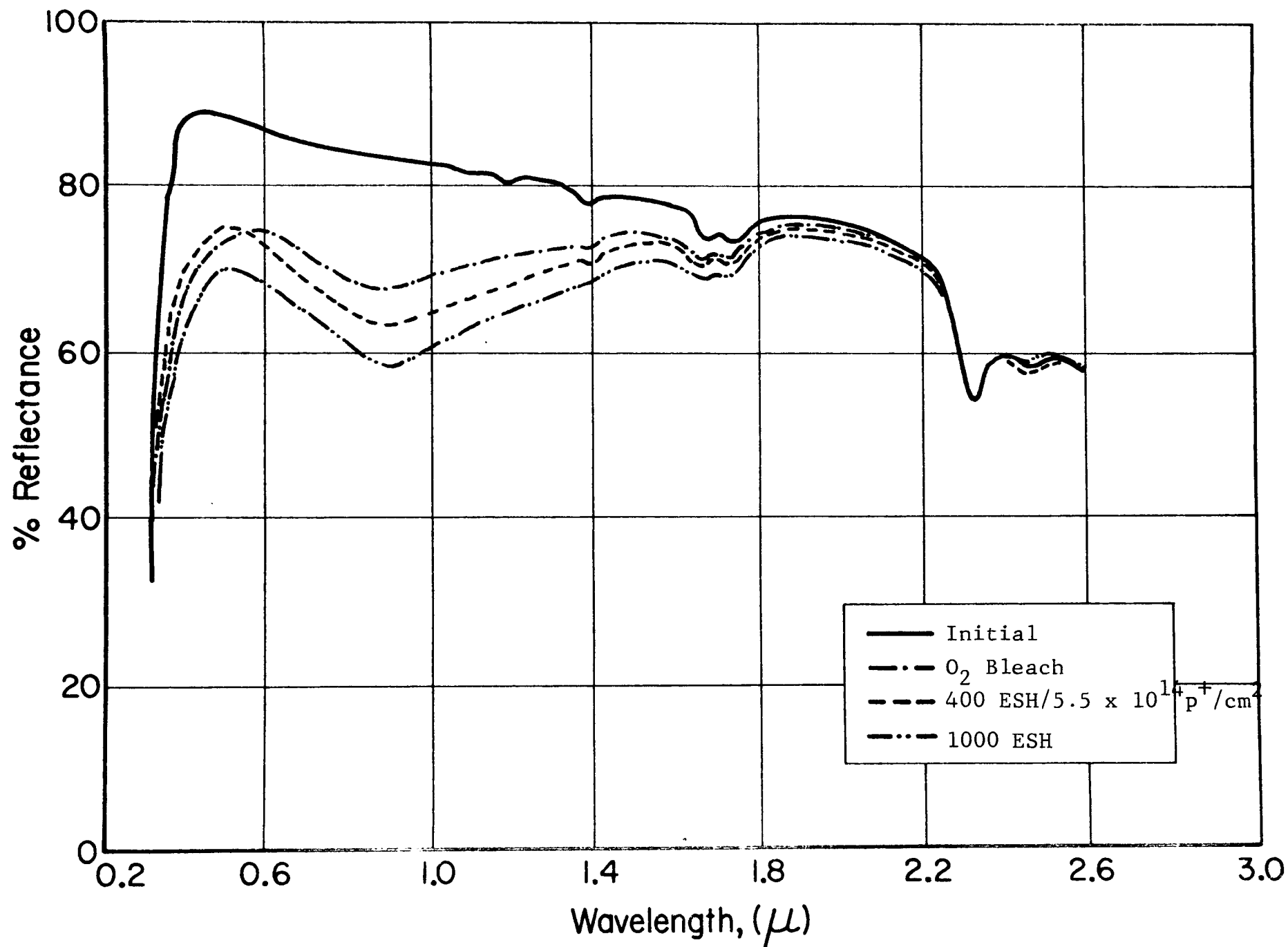


Figure 7 SPECTRAL REFLECTANCE OF  $Zn_2TiO_4:(PO_4/SiO_3/PO_4)$  (Heat Treated)/OI-650

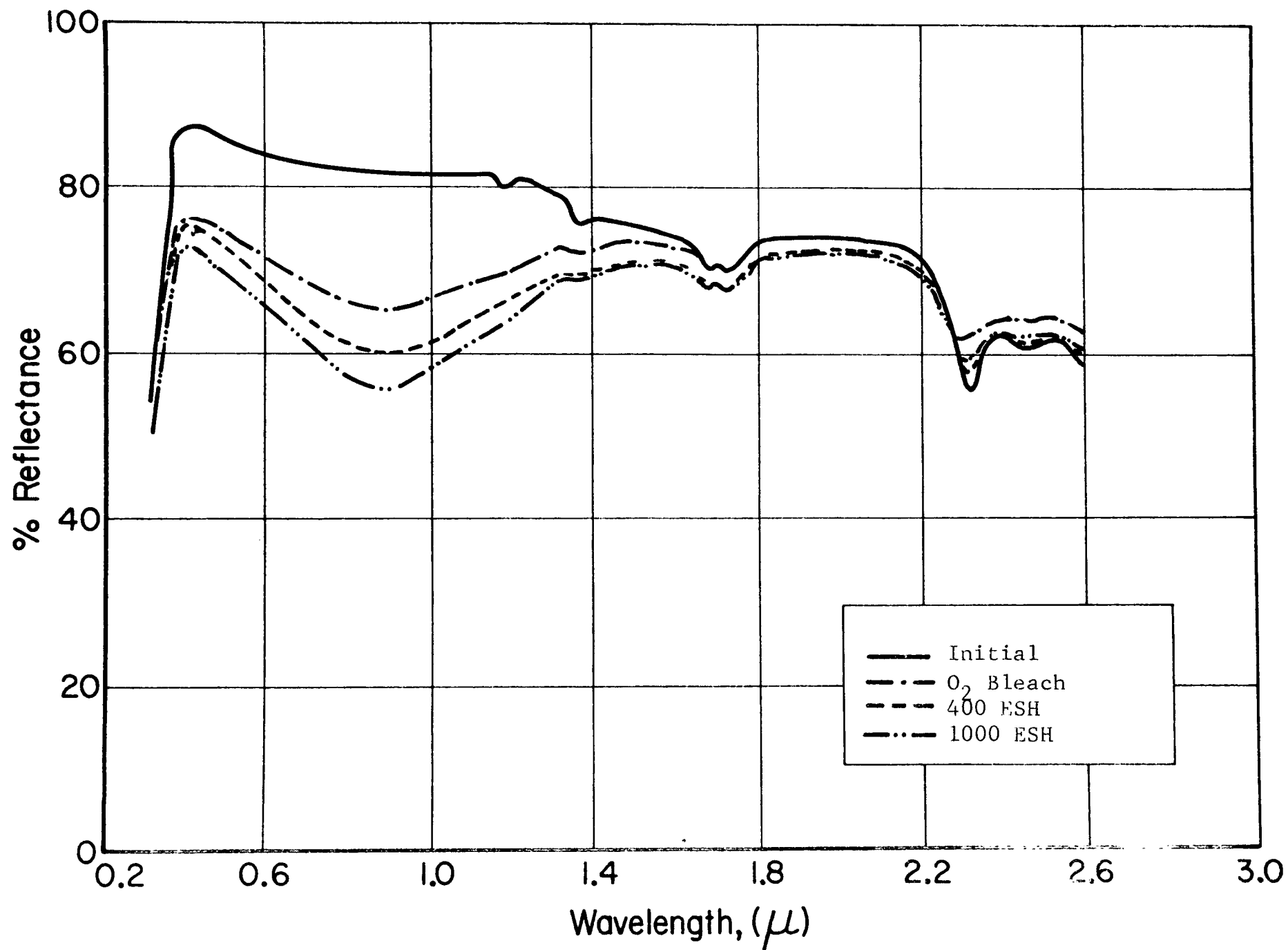


Figure 8 SPECTRAL REFLECTANCE OF  $\text{Zn}_2\text{TiO}_4:(\text{PO}_4/\text{SiO}_3/\text{PO}_4)$  (Heat Treated)/OI-650

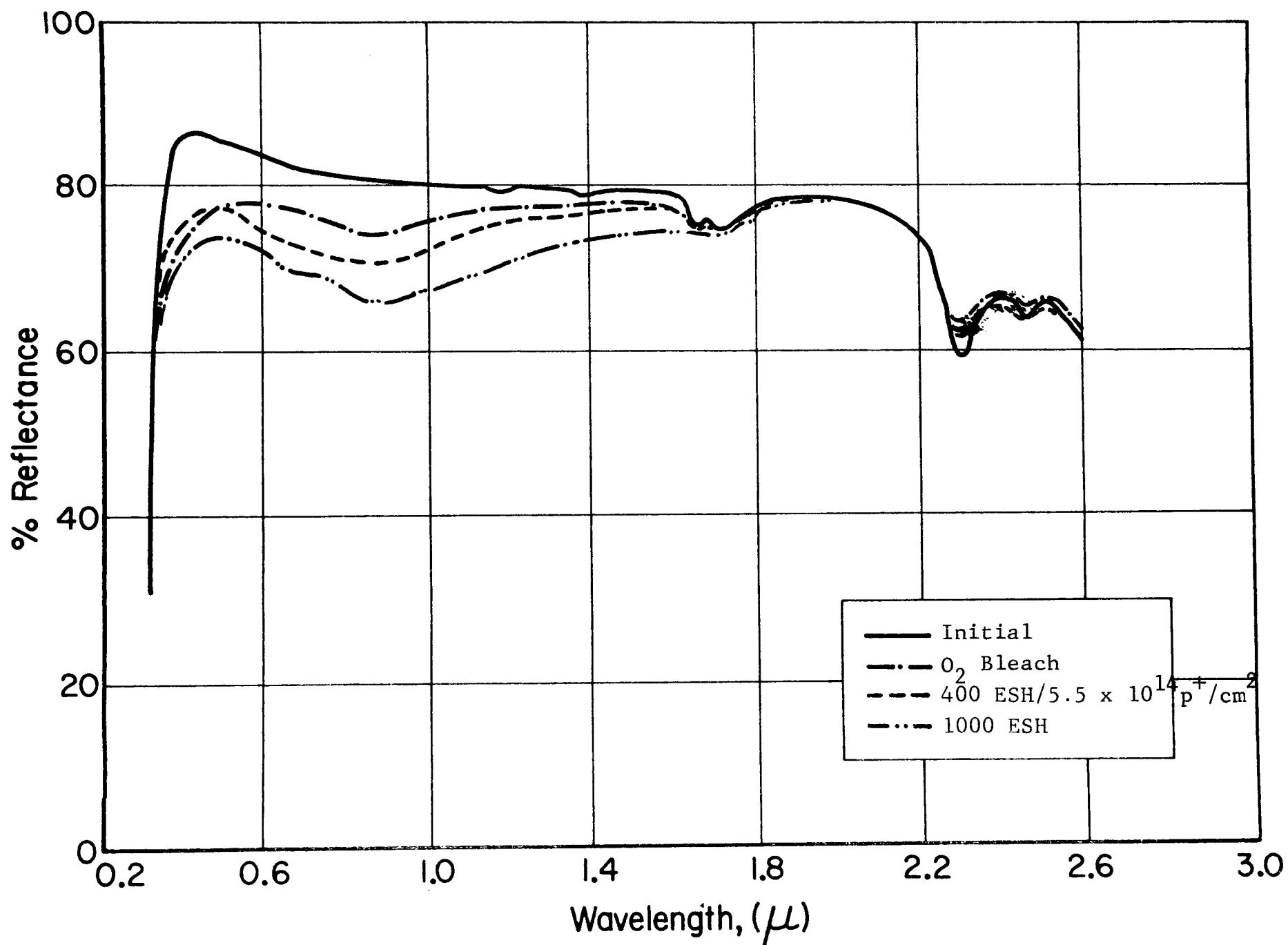


Figure 9 SPECTRAL REFLECTANCE OF  $Zn_2TiO_4:K_2SiF_6$  (Re-Heat Treated)/OI-650

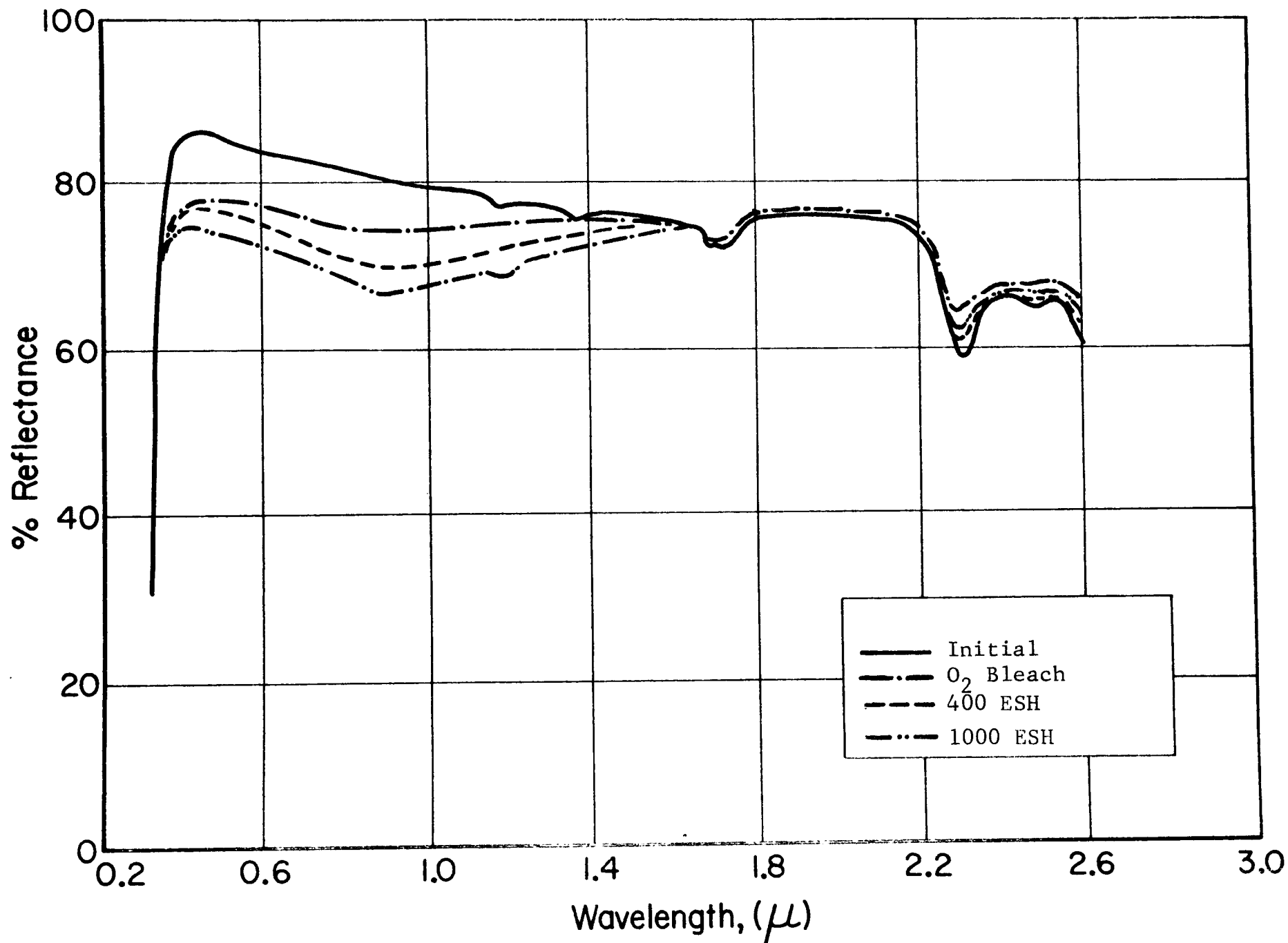


Figure 10 SPECTRAL REFLECTANCE OF  $Zn_2TiO_4:K_2SiF_6$  (Re-Heat Treated) / OI-650

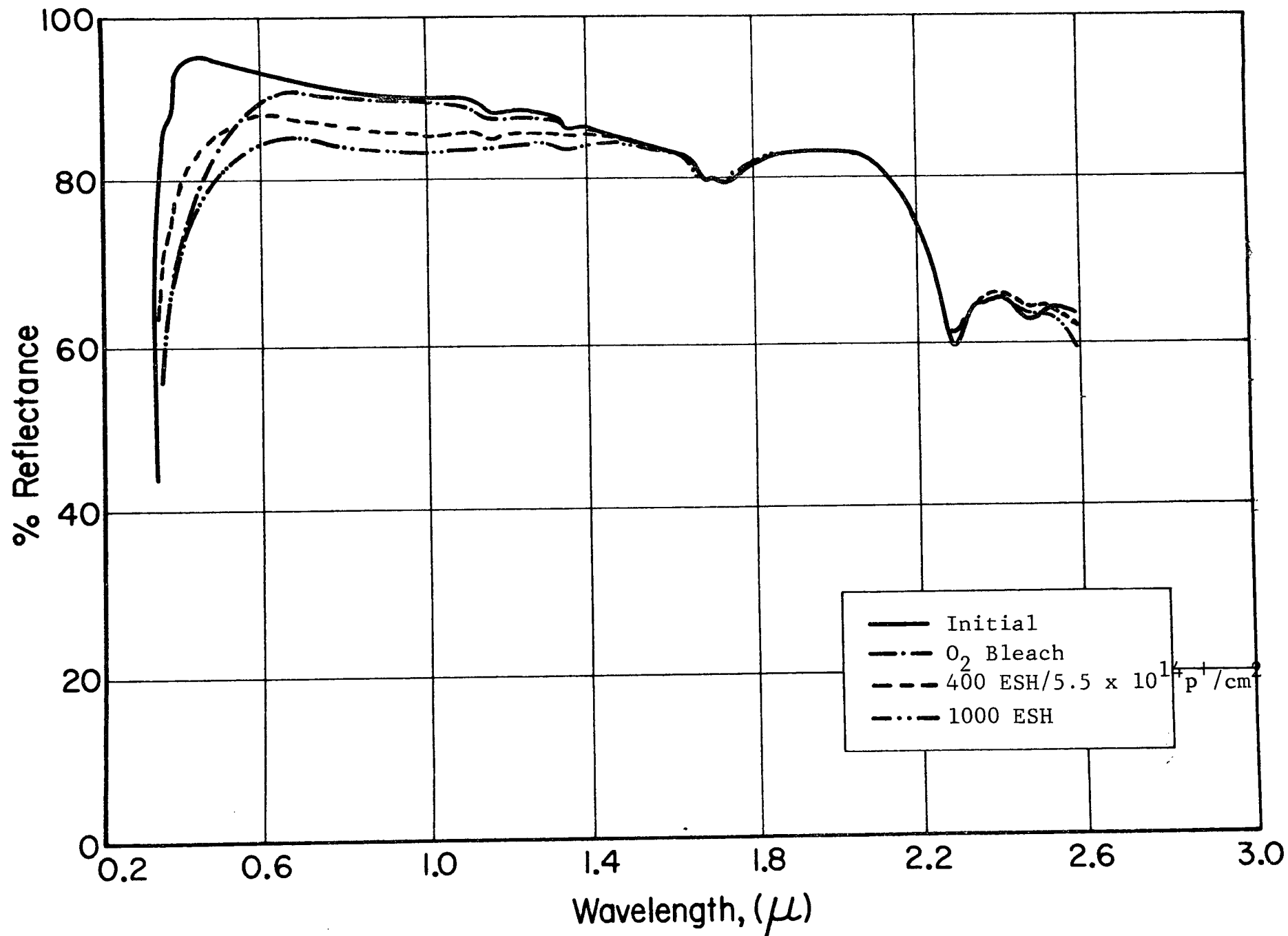


Figure 11 SPECTRAL REFLECTANCE OF  $Zn_2TiO_4:K_2SiF_6/OI-650$

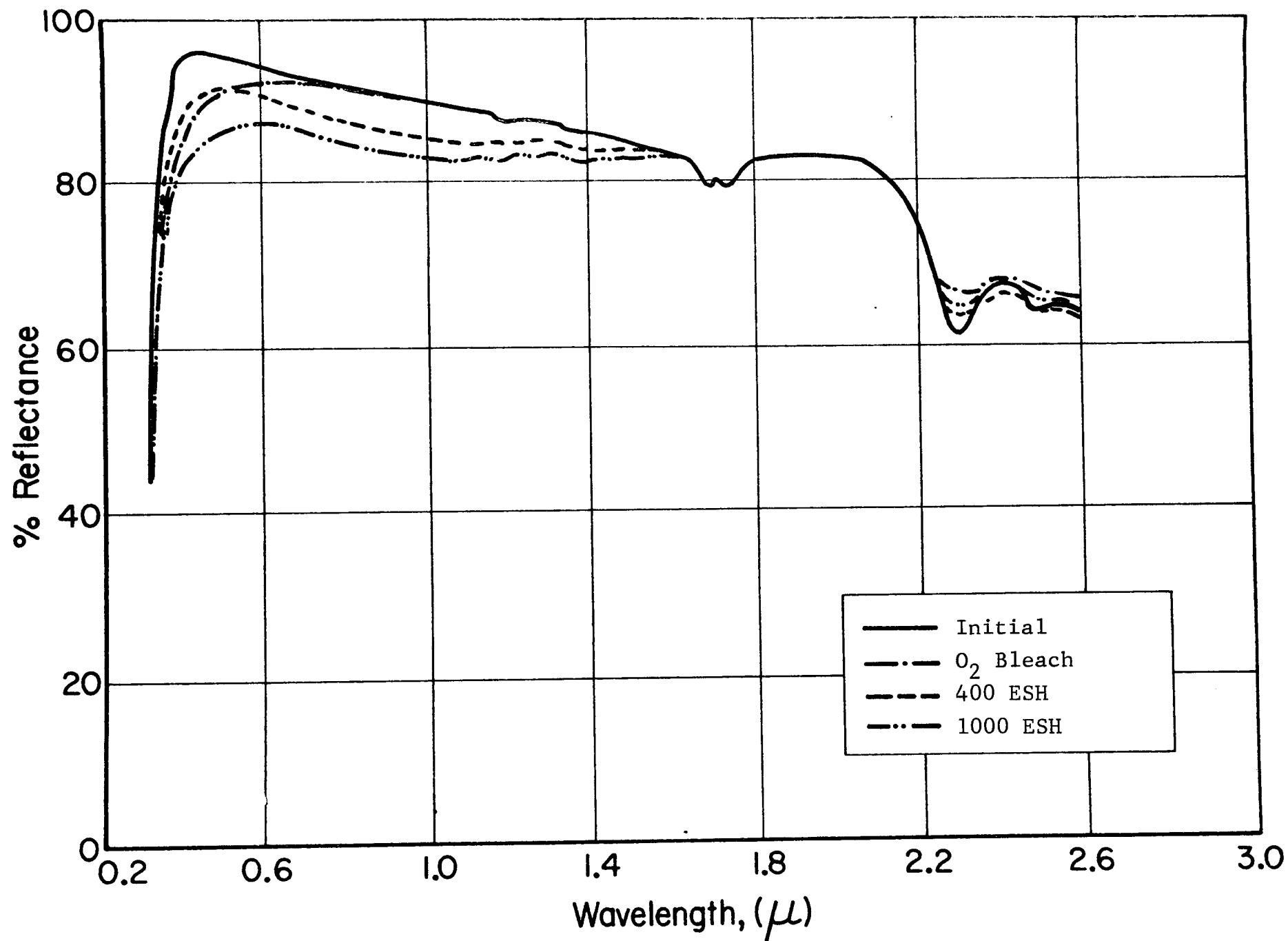


Figure 12 SPECTRAL REFLECTANCE OF  $\text{Zn}_2\text{TiO}_4:\text{K}_2\text{SiF}_6/\text{OI-650}$

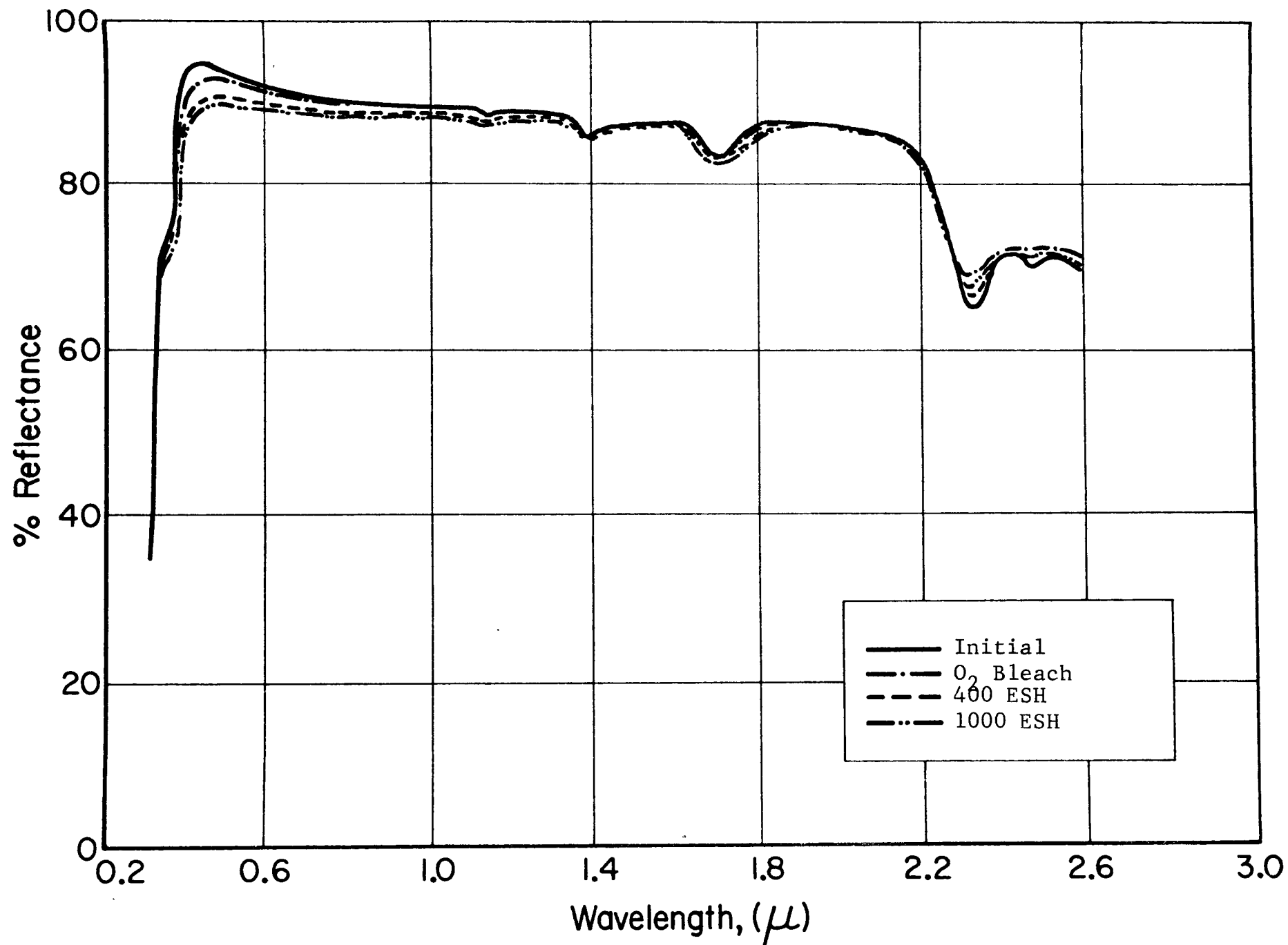


Figure 13 SPECTRAL REFLECTANCE OF  $\text{Zn}_2\text{TiO}_4:\text{K}_2\text{SiF}_6$  (Re-Heat Treated)/OI-650

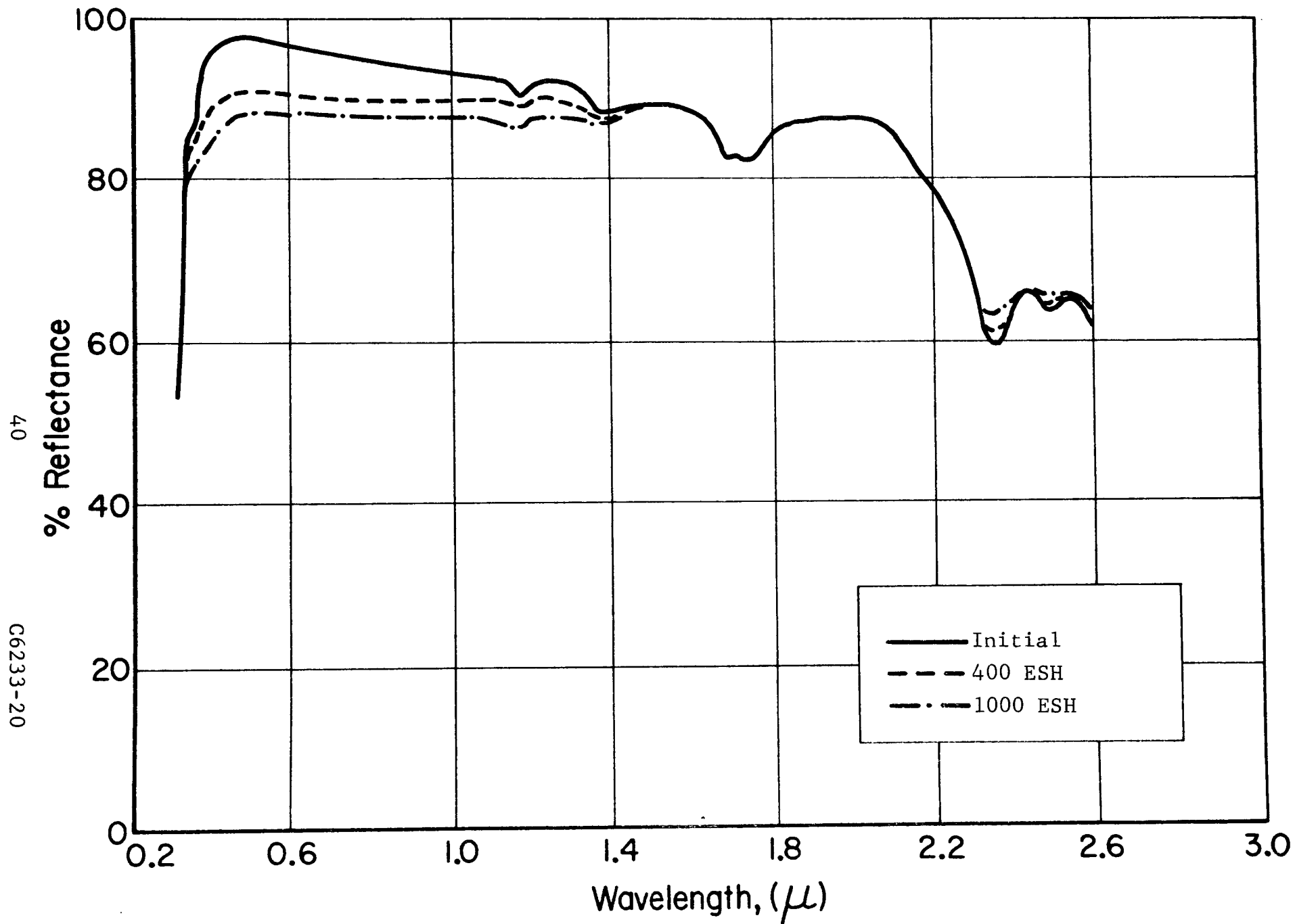


Figure 14 SPECTRAL REFLECTANCE OF  $\text{Zn}_2\text{TiO}_4:\text{LiSiF}_6/\text{OI-650}$



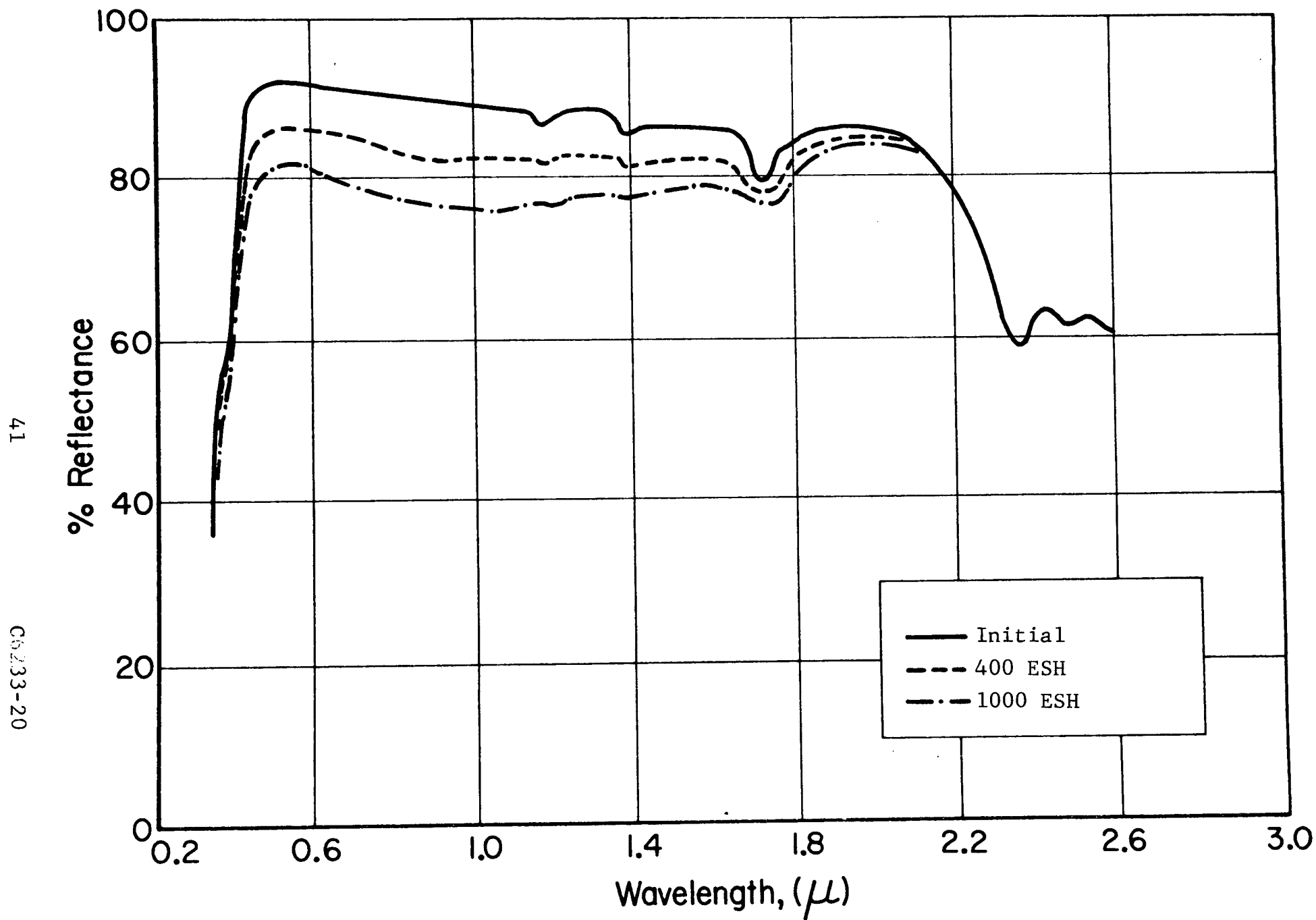


Figure 15 SPECTRAL REFLECTANCE OF  $\text{Zn}_2\text{TiO}_4\text{:LiSiF}_6$  (Heat Treated)/OI-650

to 396 ESH of ultraviolet radiation and approximately 600 EWH (Equivalent Wind Hours -  $5.5 \times 10^{14} \text{ p}^+/\text{cm}^2$ ) of simulated (1.2 keV) solar wind protons, and then to an additional 600 ESH. A part of each batch of encapsulated pigment was calcined at 1200°C/5 min. Thus the pigment in Sample No. 1 is the same as that in Sample No. 2, except for the high temperature that the pigment in Sample No. 2 received. Likewise the pigments in Sample No. 3 (heat treated) and Sample No. 4 are otherwise identical; and likewise with Sample No. 11 (heat treated) and Sample No. 10. Hence the results indicate the properties and stability of these pigments as a function of surface treatment.

Compare the spectra of sample numbers 1 and 2 (Figures 5 and 7) with those of sample numbers 7 and 8 (Figures 6 and 8). The heat treatment in the case of the phosphate-silicate surface treatment not only reduces the initial reflectance of the paint prepared from the treated pigment but predisposes it to considerable damage. Similarly, the heat treatment affects the  $\text{K}_2\text{SiF}_6$ - and  $\text{Li}_2\text{SiF}_6$ -encapsulated pigments in terms of initial properties, but its effect on stability is considerably more complicated. The spectra of proton-plus-ultraviolet irradiated samples, specimen numbers 3 and 8 (Figures 9 and 10) should be compared with those of ultraviolet irradiated (only) samples, specimen numbers 4 and 9 (Figures 11 and 12). These show the effects of encapsulation with  $\text{K}_2\text{SiF}_6$ , and of heat treatment on pigments thus encapsulated. A further comparison is afforded in Figure 13, where the pigment, also a heat-treated  $\text{Zn}_2\text{TiO}_4:\text{K}_2\text{SiF}_6$ , shows exceptional stability and a comparatively small loss of initial reflectance after heat-treatment. This latter comparison, however, not only points up the great potential that zinc orthotitanate has as a stable pigment, but it also underlines the many questions which arise in connection with process- or production-related parameters and their effects on optical properties of the pigments.

The spectra of ultraviolet-irradiated  $\text{Zn}_2\text{TiO}_4:\text{Li}_2\text{SiF}_6$  (Figures 14 and 15) further demonstrate the effects of heat treatment.

### 6.1.3 Analysis of Test Results

The properties and performance of encapsulated zinc orthotitanate pigments are very difficult to reproduce consistently. The initial optical properties and the environmental stability of pigments prepared under ostensibly identical conditions and procedures have varied considerably from batch to batch. It is, therefore, becoming increasingly important to analyze in detail the reflectance spectra of irradiated paints. In studying these spectra it is important to observe the magnitude and spectral location of environmentally induced degradation. Our analyses indicate that optical damage in zinc orthotitanate pigments develops, as a result of irradiation, in three distinct spectral locations, one of these being the familiar  $\sim 900$  nm "belly" damage.

In these analyses we have made the following assumptions. First, the environmentally-induced degradation in spectral reflectance of the paints can be attributed entirely to their respective pigments; while optical damage in the OI-650 glass resin can be created, it ordinarily contributes an insignificant amount of reflectance loss. Secondly, since the reflectance of individual paint systems are not optimum, the spectral data are to be compared on a relative, rather than an absolute basis.

For the sake of brevity and convenience, we will be referring to the defects which cause the absorption as  $T_1$ ,  $T_2$  and S. " $T_1$ " is an unbleachable defect whose presence in zinc orthotitanate causes absorption apparently centered at 360 nm. Similarly, " $T_2$ " is a defect which optically absorbs at 410 nm; it appears in some cases to be partly oxygen bleachable, though rather infrequently. The third defect is labelled "S", and is responsible for the broad "belly" absorption at about 800 nm.

In Table 8 we have compiled the spectral reflectance changes induced by exposure to a nominal 1000 ESH at each of the  $T_1$ ,  $T_2$  and S band locations. In Figure 12 (Sample No. 9) the band distinctions are clear from the plot of  $\Delta R_\lambda$  vs  $\lambda$ . From these data and from the spectral response to oxygen, some very important

Table 8

ENVIRONMENTALLY INDUCED REFLECTANCE CHANGES AT PEAK DAMAGE WAVELENGTHS  
IN ENCAPSULATED ZINC ORTHOTITANATE PIGMENTS - CREF-8

Treatment	Sample Number	$\Delta R$ (at central wavelengths)- $p^+$ + UV <sup>T</sup>						Sample Number	$\Delta R$ (at central wavelengths)-UV Only <sup>T</sup>					
		360 nm T <sub>1</sub> *	410 nm T <sub>2</sub> *	750- 900 nm S*	O <sub>2</sub> Recovery $\Delta R$	%	S Peak (nm)		360 nm T <sub>1</sub>	410 nm T <sub>2</sub>	750- 900 nm S	O <sub>2</sub> Recovery $\Delta R$	%	S Peak (nm)
:PO <sub>4</sub> /SiO <sub>3</sub> /PO <sub>4</sub>	1	.13	.15	.11	.09	82	w(855)	6	.02	.04	.05	.05	100	(795)
:PO <sub>4</sub> /SiO <sub>3</sub> /PO <sub>4</sub> - Heat Treated <sup>†</sup>	2	.13	.21	.25	.11	44	b(885)	7	.08**	.15	.24	.09	37	b(898)
:K <sub>2</sub> SiF <sub>6</sub> -Heat Treated	3	.12**	.15	.15	.09	60	b(868)	8	.11	.12	.13	.08	61	b(835)**
:K <sub>2</sub> SiF <sub>6</sub> -Heat Treated	4	.20*	.19**	.07	.06	86	w(764)	9	.16	.15	.07	.06	86	w(785)
:K <sub>2</sub> SiF <sub>6</sub> -Heat Treated	5***	.02***	.04	.01*	---	--	----							
:Li <sub>2</sub> SiF <sub>6</sub>								10	.12	.12	.07	---	--	(795)
:Li <sub>2</sub> SiF <sub>6</sub> - Heat Treated								11	.02	.07	.13	---	--	(810)

<sup>T</sup> <sup>T</sup> Total Exposure: 1032 ESH;  $5.5 \times 10^{14} p^+/cm^2$  (Samples 1-4 only)

\*T<sub>1</sub> designates band centered at 360 nm; T<sub>2</sub>, 410 nm; and S, bleachable "belly" absorption band.

\*\*Actual peak not discernible.

\*\*\*Received some  $p^+$  from spillover effect.

deductions can be made regarding the effects of encapsulation and pigment heat treatment. Heat treatment in every case increases the S-band damage, while, except in the case of the  $(\text{PO}_4/\text{SiO}_3/\text{PO}_4)$  encapsulant, it reduces damage in the  $T_1$  and  $T_2$  damage regions. Comparison of the spectra of paints prepared from heat treated pigments with those of the paints prepared from the respective precursor pigments indicates substantial reflectance losses, probably as a result of particle growth, or more probable, particle aggregation.

In Table 8 we have also listed the location of the S-peak, the spectral location of the S-band absorption maximum. Note that the actual location of the peak varies from about 760 nm (1.6 eV) to nearly 900 nm (1.4 eV), and that inevitably the greater the S-band damage, the longer the wavelength at which it peaks. This variable location of the band peak implies a shifting of one energy state with respect to another, probably because of band bending during irradiation. The S-band may in itself, because of this and other observations, result from two different surface defects. The spectral reflectance values of the S-band after exposure to one atmosphere of pure  $\text{O}_2$  reveal that bleaching occurred in every case, but that there was always substantially less reflectance recovery in paints with heat-treated pigments, and in those paints with non heat-treated pigments the residual S-band damage was attributed to the low energy wing of the intense  $T_2$  band. The lack of full (or nearly full) S-band recovery in heat-treated pigments suggests that the heat treatment stabilizes surface defects by causing them either to interact more completely with the encapsulant or to diffuse more deeply into the pigment particles. With the exception of the phosphate/silicate/phosphate encapsulant system, heat treatment reduces bulk damage, i.e., in the  $T_1$  and  $T_2$  bands.

The relatively greater effects of protons were as expected. The spectra of identical samples, one irradiated with ultraviolet plus protons, and one with ultraviolet only, suggest that the

protons create substantial bulk damage but have little, if any effect on surface (S-band) damage, as evidenced by the  $\Delta R_\lambda$  values at the S-band in comparable samples (e.g., No. 4 vs No. 9). Another interesting analysis is that of the relative development of the  $T_1$  and  $T_2$  bands. In general the  $T_2$  center is at least as sensitive to irradiation as the  $T_1$  center. From the magnitudes of the  $\Delta R_\lambda$  values at the  $T_1$  and  $T_2$  absorption bands it is quite probable that the two are produced in a proportion which is at least partly controlled by the surface encapsulant and partly by the heat treatment conditions. For instance, the  $\Delta R_\lambda$  values for the  $T_1$  and  $T_2$  bands of  $\text{Zn}_2\text{TiO}_4:(\text{PO}_4/\text{SiO}_3/\text{PO}_4)$  show that both are sensitive to proton irradiation - hence are probably due to defects which are created by induced atomic rearrangements; these data also show that the same conclusion may be drawn in comparing the developments of the  $T_1$  and  $T_2$  bands in paints with heat-treated vs those with non heat-treated pigments.

Finally, it must be noted that these paints sustained relatively high degradation. From the development patterns of the three bands the causes would appear to be intrinsic defects, although surface contamination can not be completely ruled out. This argument is augmented by the fact that heat treating tends to reduce  $T_1$  and  $T_2$  developments in silicofluoride encapsulated pigments, to increase them in phosphate encapsulated pigments, and in all pigments to promote S-band development. This means that different surface treatments can and do cause large and very different damage effects.

#### 6.1.4 Conclusions

An unusually large amount of optical degradation has occurred in the paint samples; it is very likely due to intrinsic defects - possibly because of a formulation error or a malfunction in the processing equipment (e.g., a temperature measurement). Although anomalous in magnitude, the degradation spectra are characteristic. Analyses of the spectra tend to rule out contamination in the test system as an explanation. Contamination of the samples during their preparation remains a possibility, but it cannot account for

most of the performance trends observed. Looking at the effects of heat treatment on S-band stability, we can conclude that, if these are stoichiometric defects on the surface, heat treatment greatly amplifies their already deleterious effect. Consequently, stoichiometry must be carefully controlled, not only because it affects the development of the  $T_1$  and  $T_2$  bands, but because of the very large S-band instabilities generated by any subsequent heating.

## 6.2 IRIF Test I-55

### 6.2.1 Background

The development of a stable paint based on zinc orthotitanate and OI-650 glass resin depends not only upon the development of each of these two as stable components individually, but upon the elimination of interactions between them which lead to instabilities (mainly in the S-band). This particular test was conducted to determine individual properties and performance data, to compare components prepared in different ways. The performance of these components as paints was determined in CREF Test No. 8 discussed in the preceeding section.

The samples were irradiated in the IRIF-I facility with simulated solar radiation from a PEK A-H6 mercury-argon compact source. The intensity was approximately 6 ultraviolet suns at the sample location; the total exposure was 1000 ESH. Sample temperatures were maintained at approximately 12-15°C. Table 9 lists the samples and their descriptions.

### 6.2.2 Results of Test

The spectral reflectance curves are presented in Figures 16-23. The first five of which are spectra of zinc orthotitanate powders. Except for Sample No. 1, the latter powders are the pigments in the OI-650 paints irradiated in CREF Test No. 8. Generally, all of the B-229 type zinc orthotitanate pigments appear to be quite stable, sustaining only a small fraction of the damage occurring in their OI-650 paints.

Table 9

SAMPLE DESCRIPTIONS  
IRIF TEST NO. I-55

Sample (Position) Number	Sample Description	Figure Number
1	$\text{Zn}_2\text{TiO}_4$ Y/4 (coprecipitation method)-900°C/8 hr	20
2	OI-650 glass resin, standard, air dried	21
3	OI-650G (Batch C-400), air dried	22
4	OI-650G (Lot 34-2), air dried	23
5	$\text{Zn}_2\text{TiO}_4$ , untreated, Batch C-316 (B-229 method)	16
6	$\text{Zn}_2\text{TiO}_4$ *:( $\text{PO}_4/\text{SiO}_3/\text{PO}_4$ )-heat treated 1200°C/5 min.	17
7	$\text{Zn}_2\text{TiO}_4$ *: $\text{Li}_2\text{SiF}_6$ -heat treated 1200°C/5 min.	19
8	OI-650G, cured 150°C/1 hr	26
9	OI-650G, cured overnight at 80°C	25
10	OI-650, cured overnight at 80°C	24
11	$\text{Zn}_2\text{TiO}_4$ *: $\text{K}_2\text{SiF}_6$ -heat treated 1200°C/5 min	18
12	Blank	

\* $\text{Zn}_2\text{TiO}_4$ , from batch C-316.



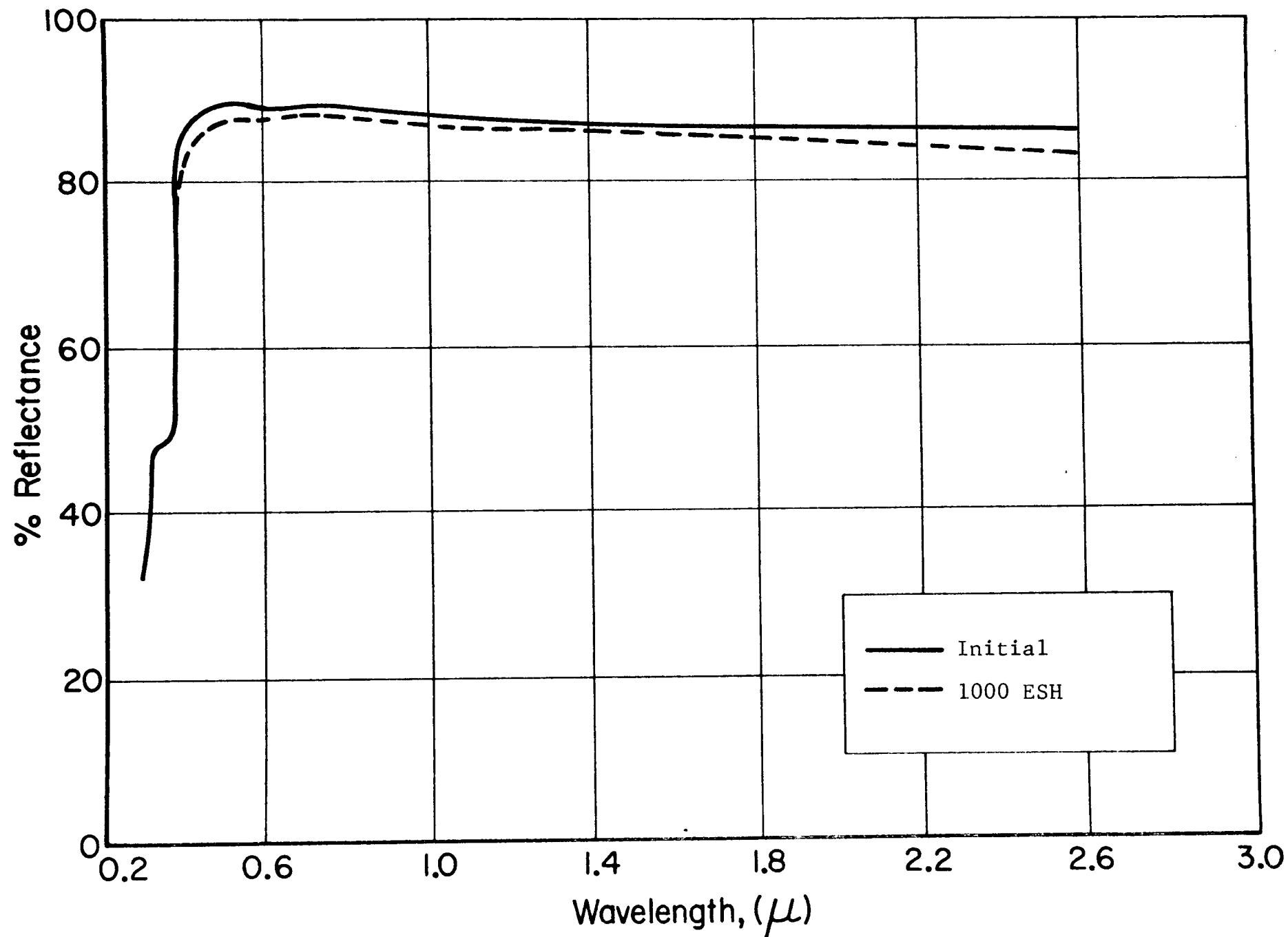


Figure 16 SPECTRAL REFLECTANCE OF  $\text{Zn}_2\text{TiO}_4$ : (Untreated B-229 METHOD)

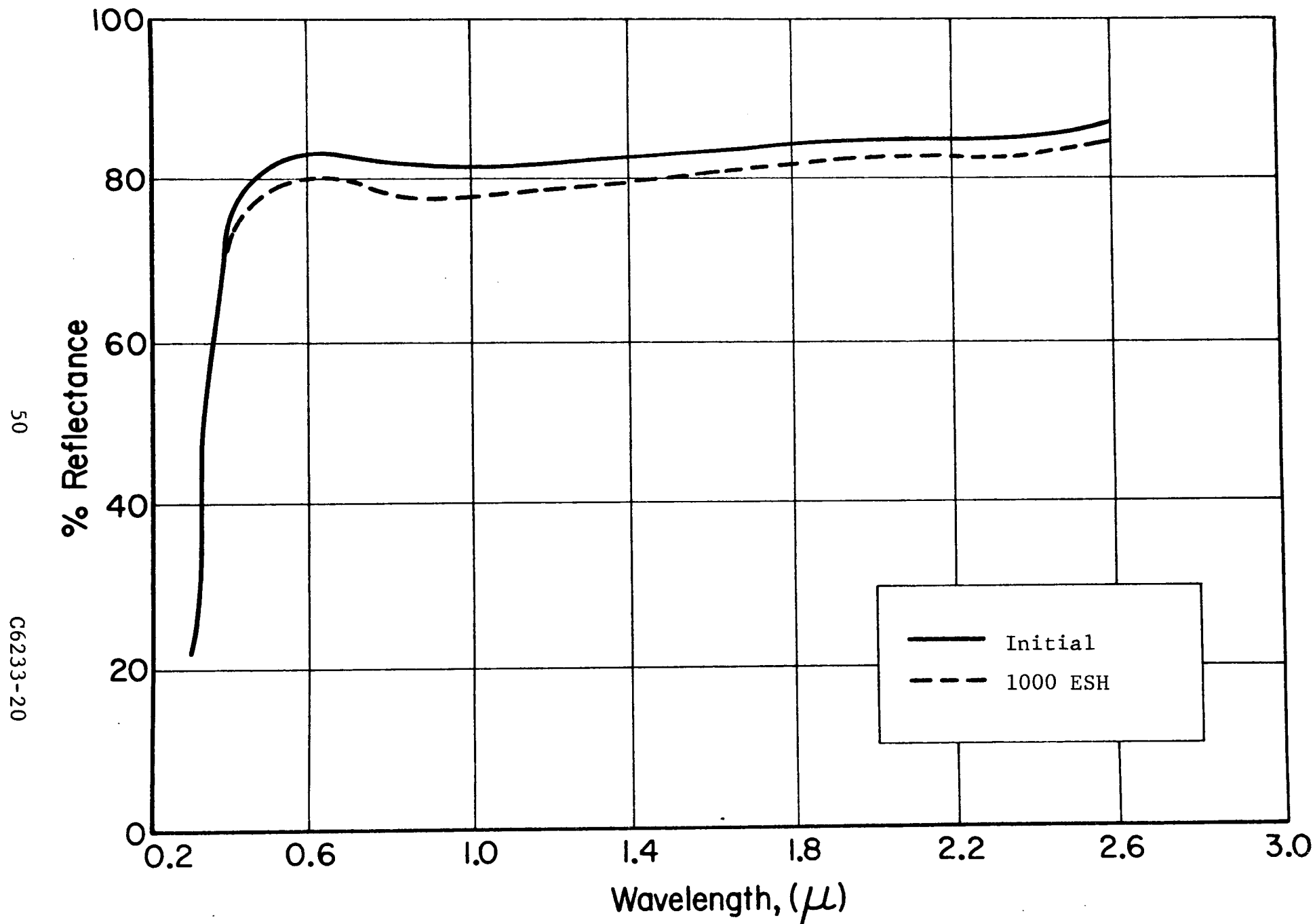


Figure 17 SPECTRAL REFLECTANCE OF  $\text{Zn}_2\text{TiO}_4:(\text{PO}_4/\text{SiO}_3/\text{PO}_4)$  (Heat Treated)

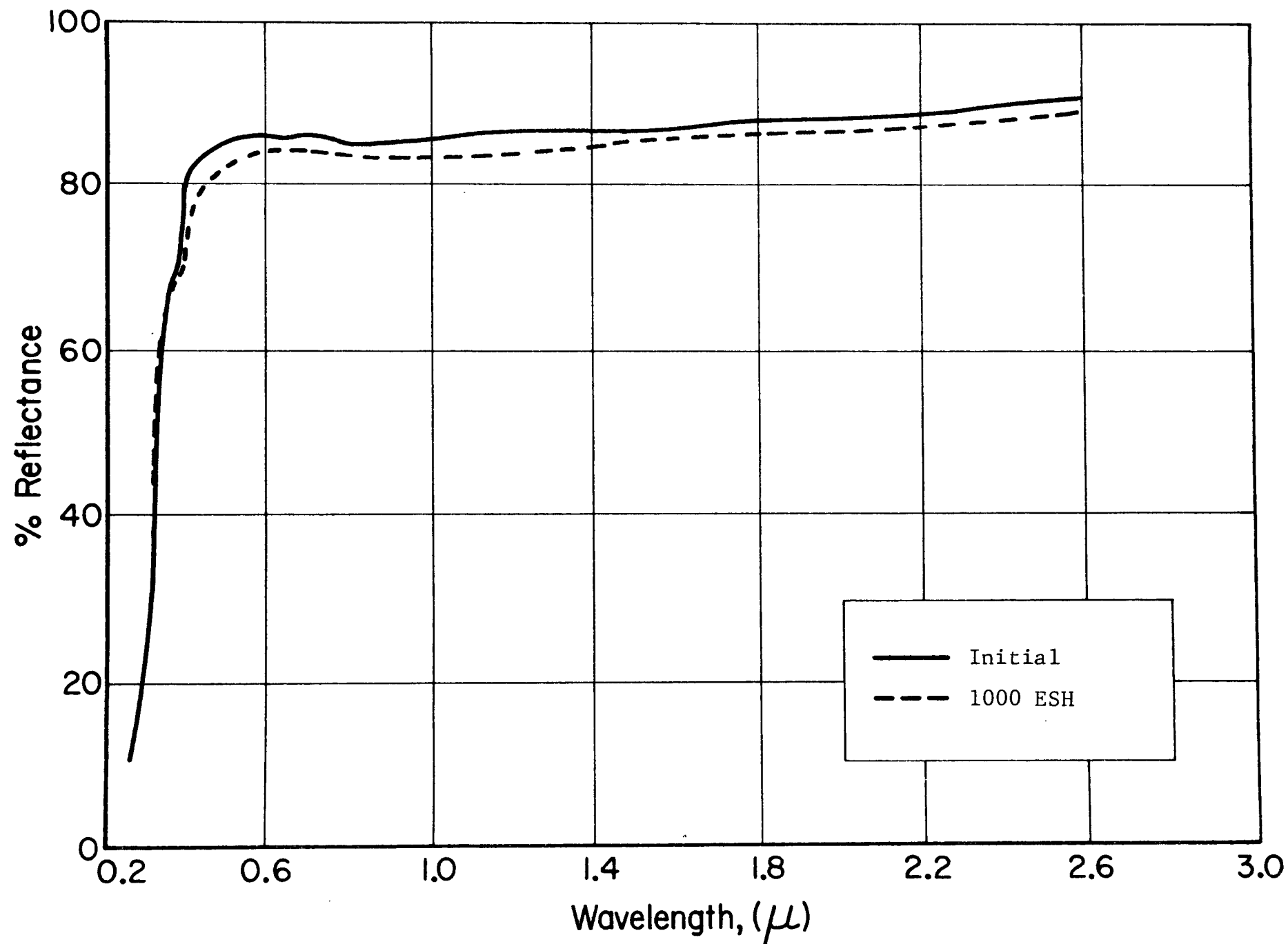


Figure 18 SPECTRAL REFLECTANCE OF  $\text{Zn}_2\text{TiO}_4:\text{K}_2\text{SiF}_6$  (Heat Treated)

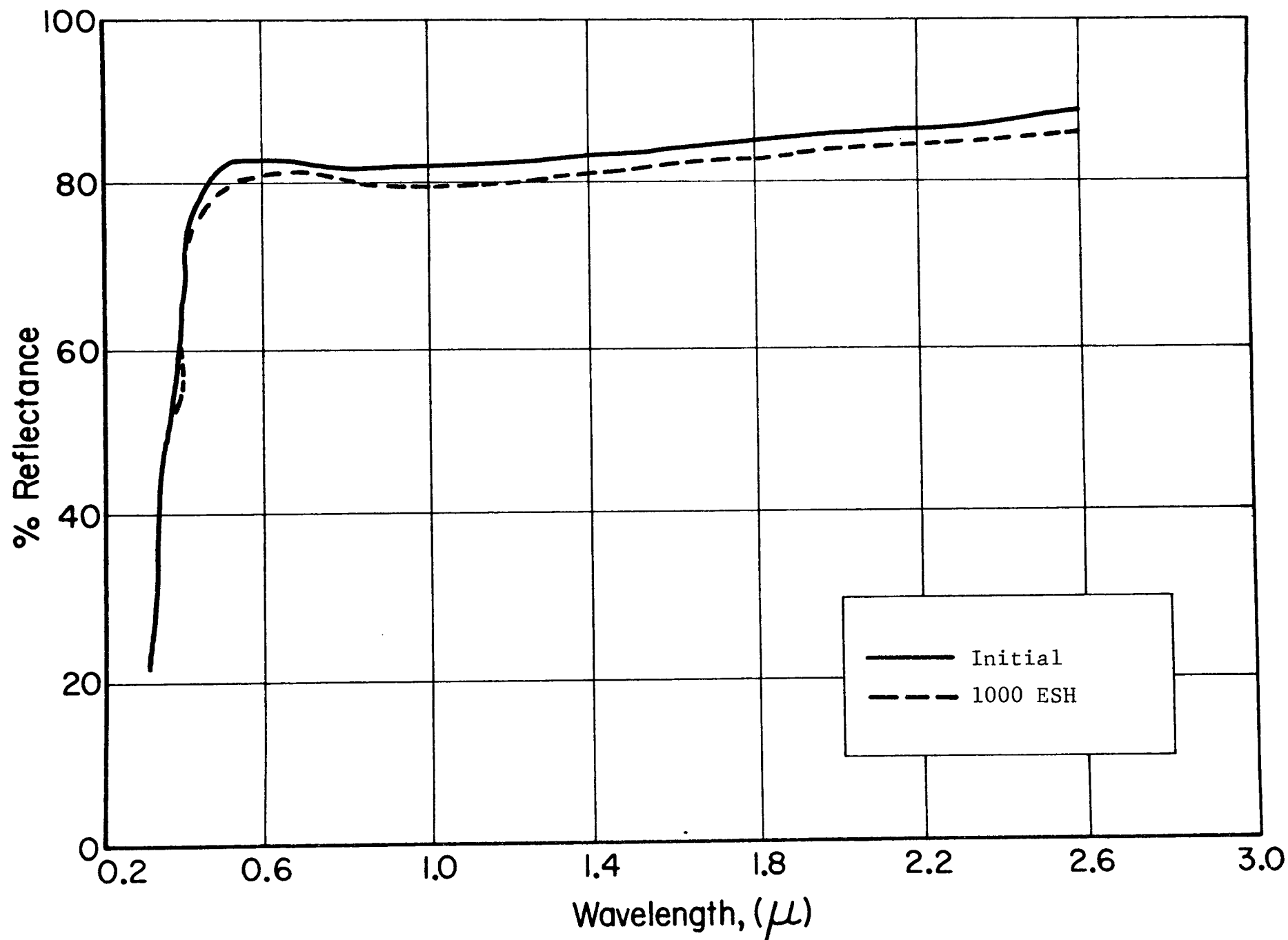


Figure 19 SPECTRAL REFLECTANCE OF  $\text{Zn}_2\text{TiO}_4:\text{LiSiF}_6$  (Heat Treated)

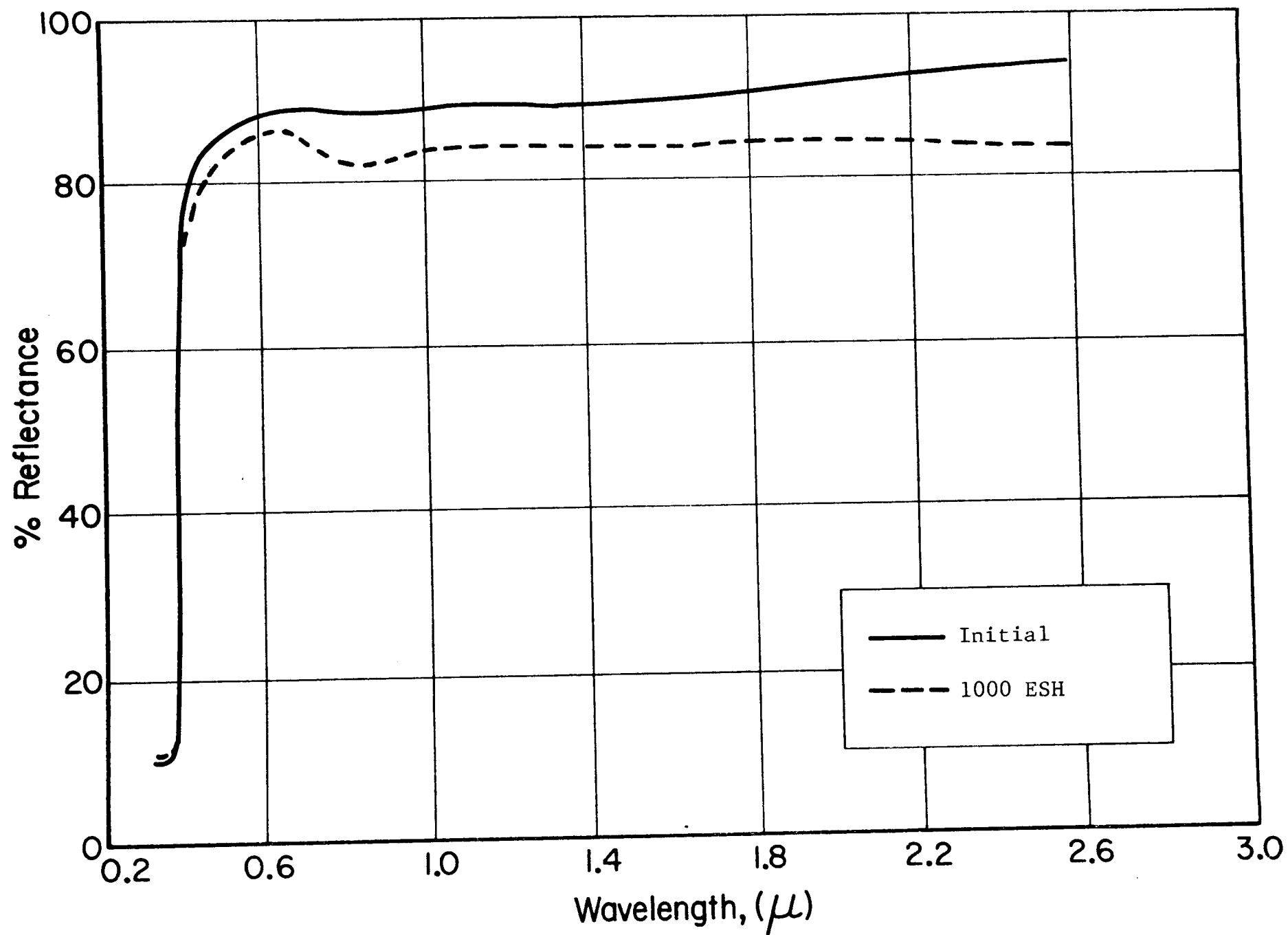


Figure 20 SPECTRAL REFLECTANCE OF  $\text{Zn}_2\text{TiO}_4$  (UN-TREATED COPRECIPITATION METHOD)

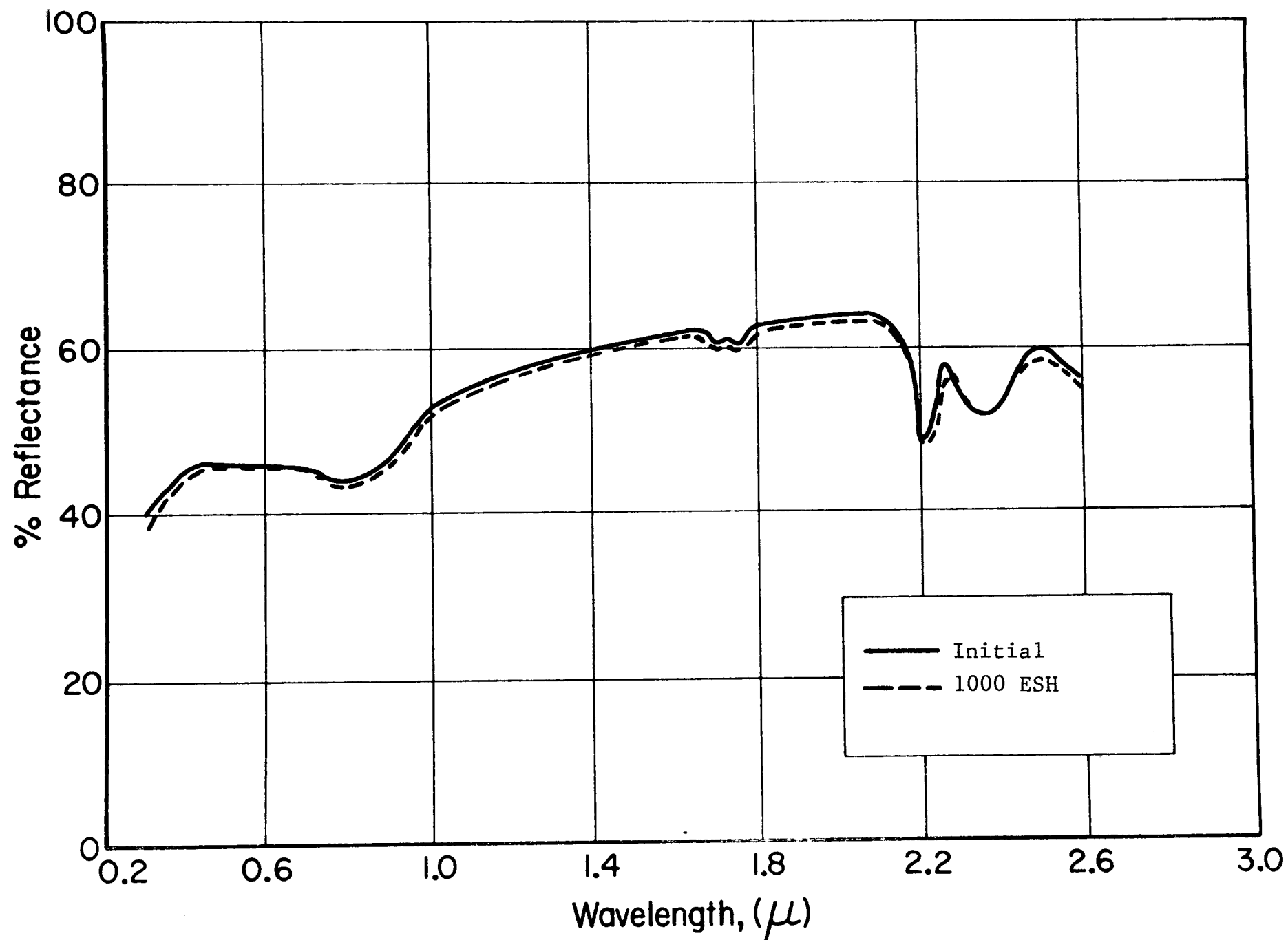


Figure 21 SPECTRAL REFLECTANCE OF OI-650 GLASS RESIN (STANDARD), AIR DRIED

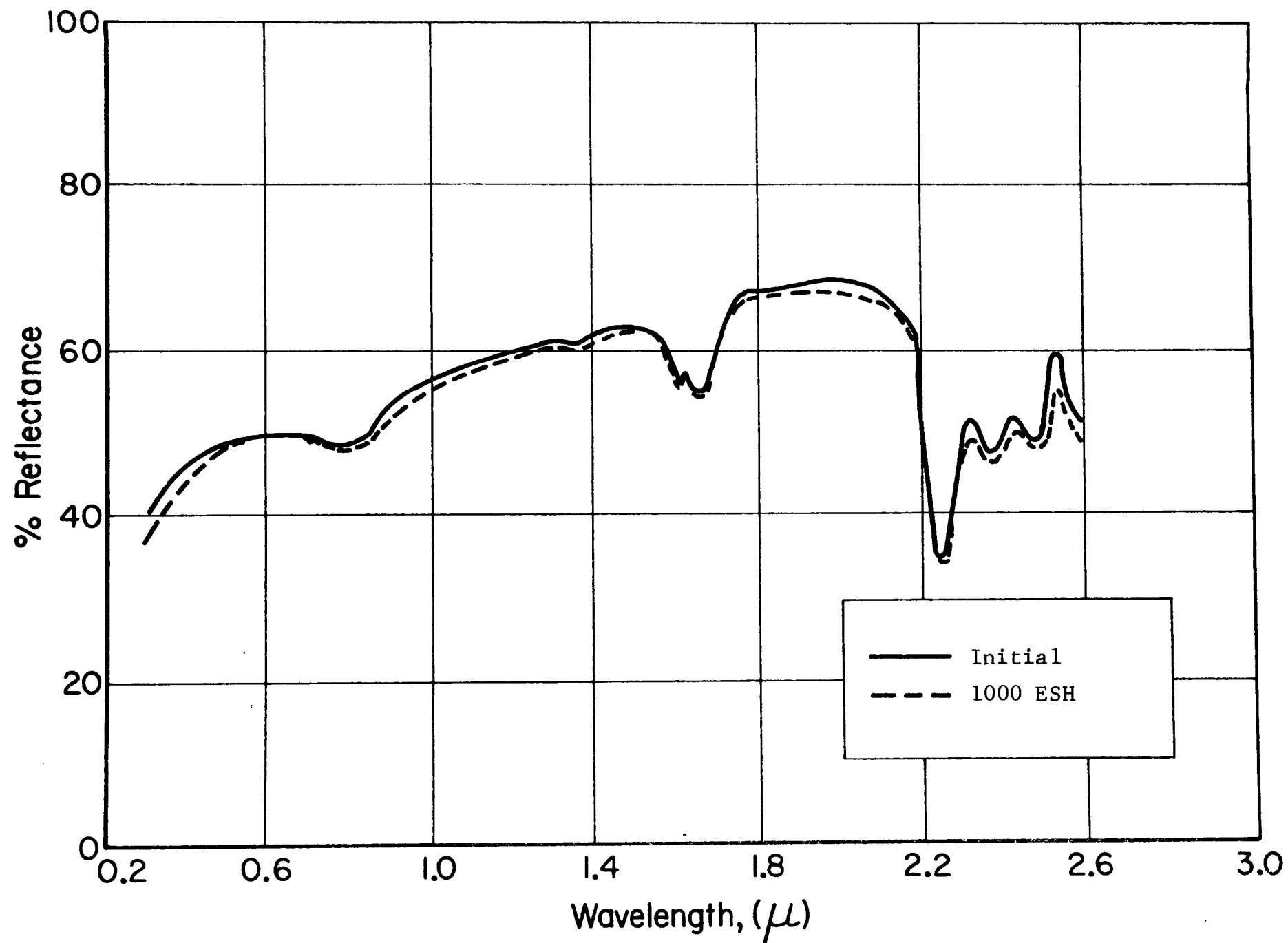


Figure 22 SPECTRAL REFLECTANCE OF OI-650G (BATCH C-400); AIR DRIED

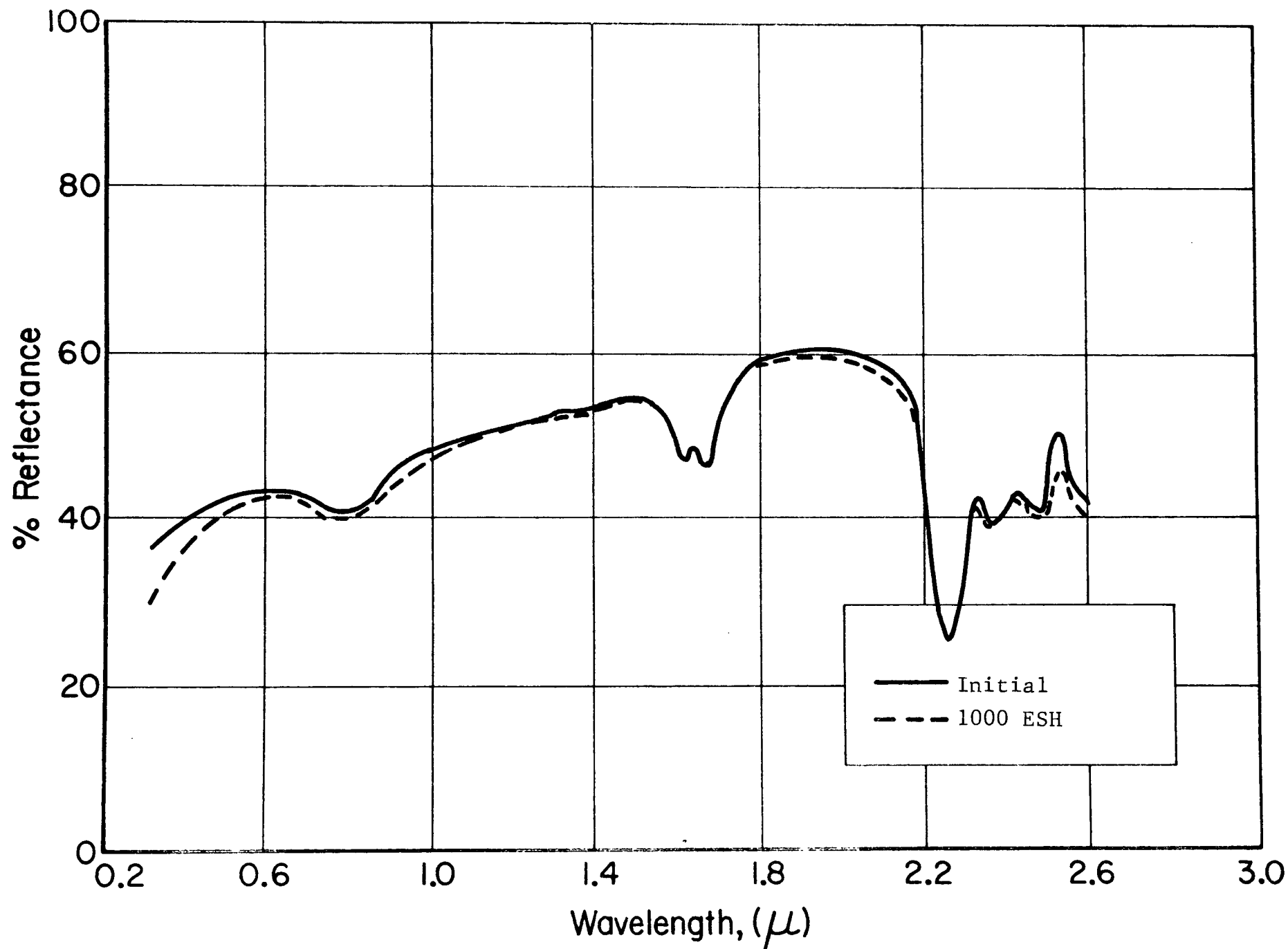


Figure 23 SPECTRAL REFLECTANCE OF 01-650G (LOT 34-2); AIR DRIED



In terms of the bands previously defined, unencapsulated, "raw" (un-heat treated) zinc orthotitanate (Figure 16) displays no  $T_1$  development, a slight  $T_2$  development, and a perceptible S-band. The stair-step structure of reflectance in the ultraviolet region characterizes the ZnO excess of this compound. The phosphate/silicate/phosphate pigment (heat-treated at 1200°C/5 min) whose spectra are shown in Figure 16, indicates definite developments in all three bands. Very much like those of the raw zinc orthotitanate powder, the spectra of the pigment  $Zn_2TiO_4:K_2SiF_6$  (1200°C/5 min) in Figure 17 exhibit no  $T_1$  development, but definite  $T_2$ - and S-band development. The lithium silicofluoride encapsulated pigment (also heat-treated at 1200°C/5 min) (Figure 19) displays similar stability, with the same remarks applying also to the absorption band development. The pigment whose reflectance spectra are shown in Figure 20 was prepared by firing at 900°C/8 hr the coprecipitation product of the chlorides of zinc and titanium from an aqueous oxalic acid solution. The spectra clearly reveal the presence of ZnO; the characteristic ultraviolet-induced free carrier (I.R.) absorption and the very sharp absorption edge at 376 nm unmistakably point to a significant excess of ZnO in this pigment - an observation consistent with the x-ray interpretations. The S-band development is also somewhat pronounced. The performance, if compared to that of B-229 method pigments, would not be good; but, on the basis that it is produced using a completely experimental method, the properties and performance are both very encouraging.

The spectra in Figures 21-26 are the reflectance spectra of thin films of Owens-Illinois glass resin applied to IRIF coupons. Thus, the important feature to notice is the ultraviolet induced absorption, as indicated by a loss in reflectance; the absolute reflectance values are not relevant. Since the films were all applied at nearly the same thickness, the induced absorptance, as inferred from the reflectance loss, will be indicative of each material's stability. The IITRI modified OI-650 glass resin is designated OI-650G. In Figure 21 are the spectra of (standard)

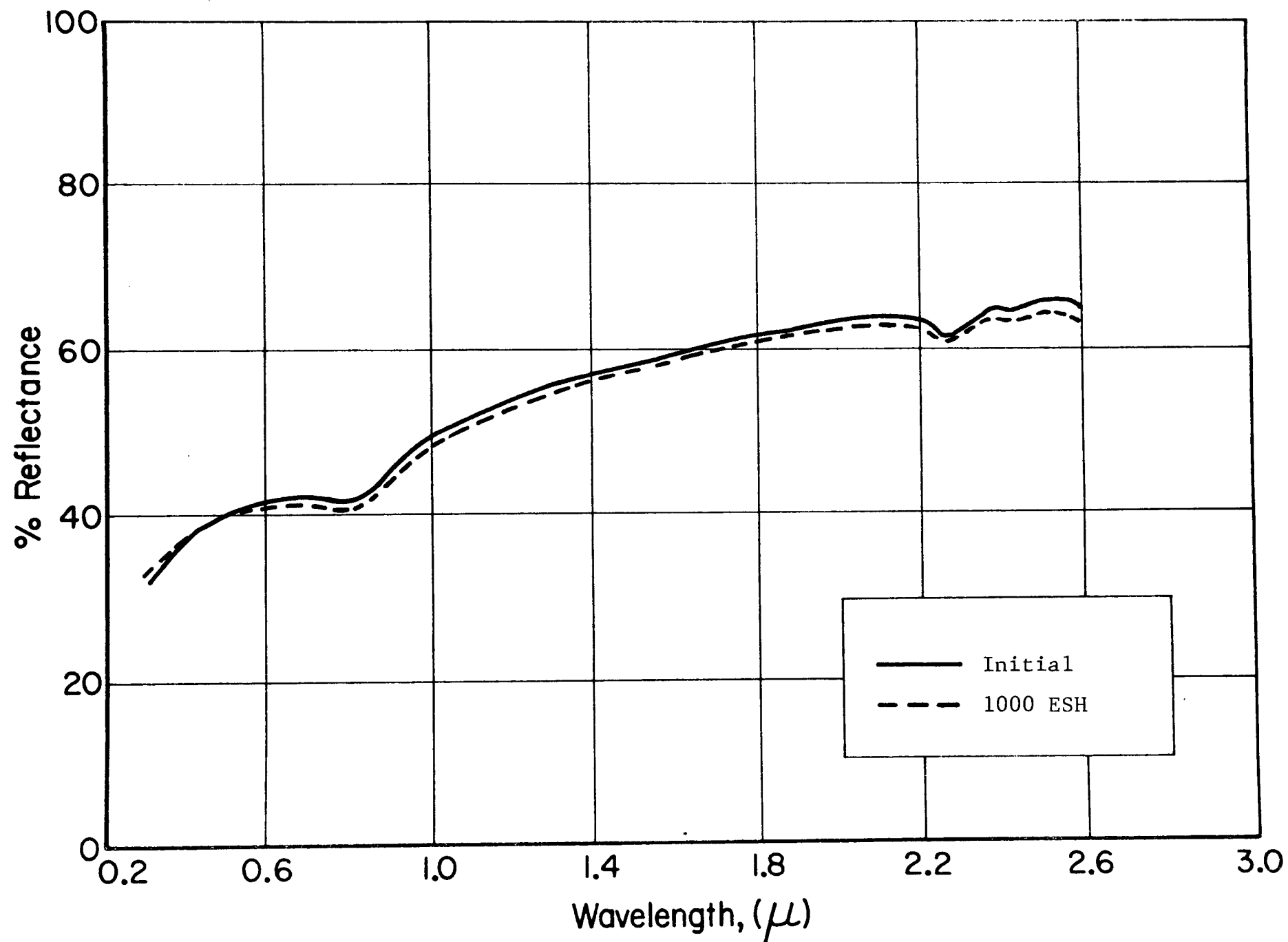


Figure 24 SPECTRAL REFLECTANCE OF OI-650; CURED 16 HRS @ 80°C

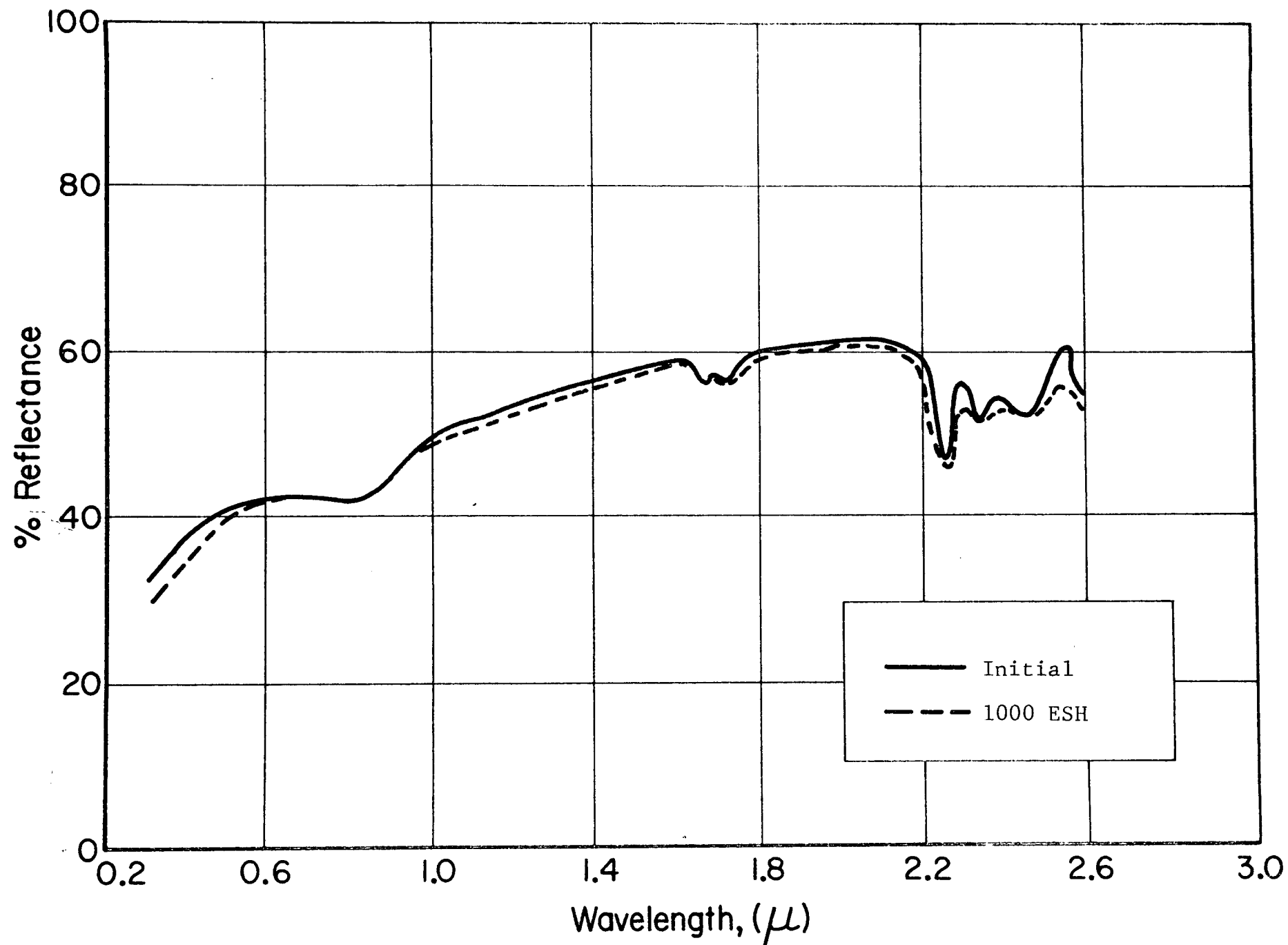


Figure 25 SPECTRAL REFLECTANCE OF OI-650G; CURED 16 HRS @ 80°C

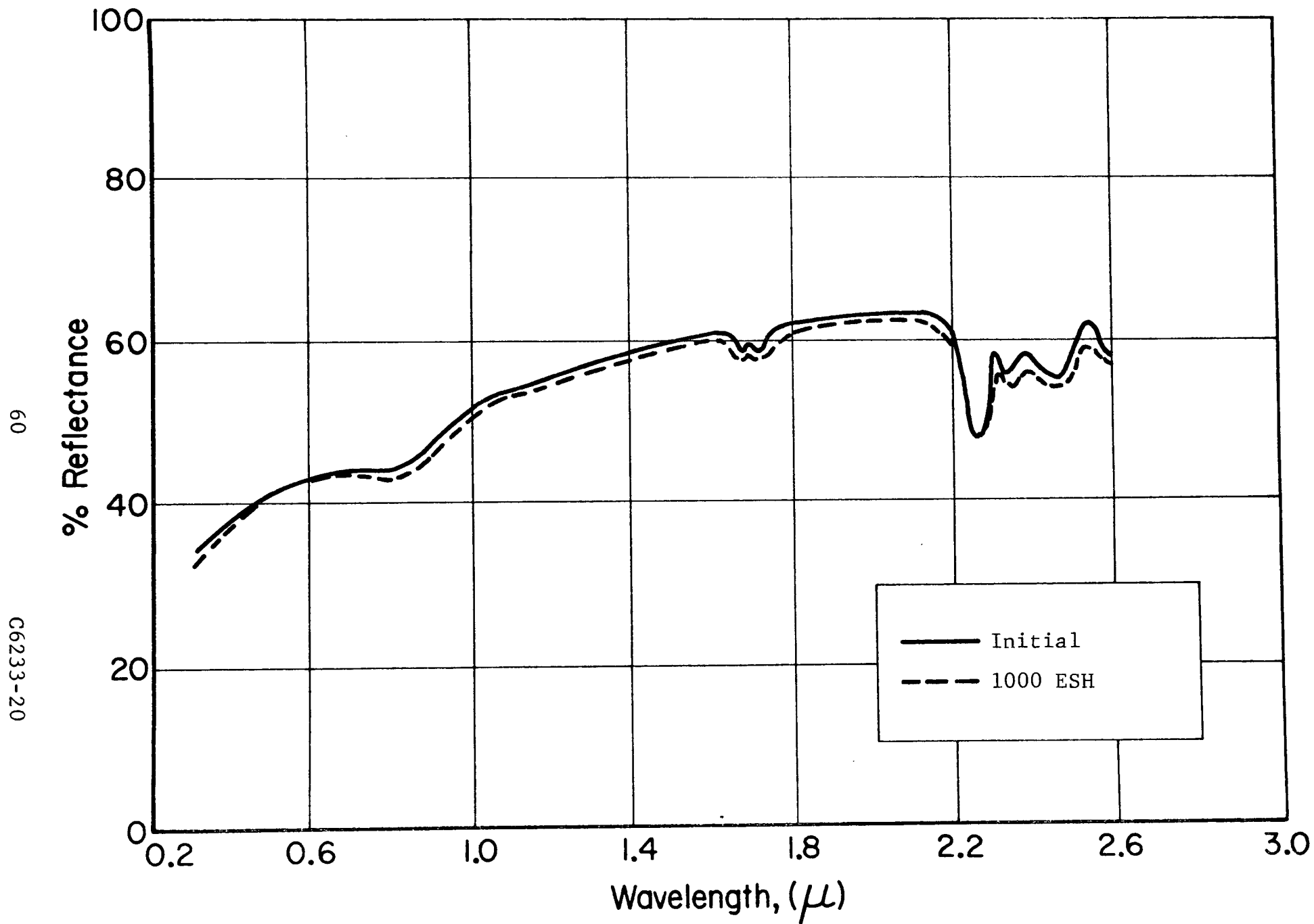


Figure 26 SPECTRAL REFLECTANCE OF OI-650G; CURED 1 HR @ 150°C

OI-650, air dried. The spectra of two different lots of air dried films of OI-650G are presented in Figures 22 and 23. An analogous set is shown in Figures 24-26. Figure 24 shows the spectra of OI-650 cured overnight at 80°C, while Figure 25 shows them for OI-650G also cured overnight at 80°C. The reflectance spectra of an OI-650G film cured at 150°C/1 hr are given in Figure 26. All of these films are exceptionally stable, especially those that have been heat cured.

### 6.2.3 Conclusions

The magnitude of optical damage in OI-650G is very small. The results thus show that the IITRI-modified OI-650 glass resin (i.e., OI-650G) is as inherently stable as the standard product and that this stability is increased by heat curing. Taken together with results of many previous irradiation studies, these results make it clear that this inherent stability has not exhibited significant batch-to-batch variations.

The performance of the zinc orthotitanate pigments in this test demonstrates that they all are basically stable. Their performance in CREF Test No. 8, where they were tested in the form of OI-650 and OI-650G silicone paints, however, emphatically points up the deleterious interaction between the pigment and the vehicle. The nature of this interaction appears to have an effect on the pigments' bulk properties as well as on its surface properties. The effect of this interaction on bulk properties is witnessed in the development of the  $T_1$  and  $T_2$  bands; in the case of the paint these bands are strongly developed, in the pigment alone they are scarcely detectable. The fact that these bands exist in the spectra of irradiated pigment powders and not in those of clear resin films allows the tentative conclusion that the resin-pigment interaction affects the pigment and not the resin.

### 6.3 IRIF Test I-57

#### 6.3.1 Background

There are current and pressing requirements for a paint system more stable than S-13G and yet available in large quantities. Accordingly, we have developed a paint system utilizing OI-650G as the vehicle and our potassium silicate encapsulated zinc oxide as the pigment. As indicated earlier this paint system has been designated A-429M.

Samples of this paint system have been irradiated in IRIF Test I-57 and also in a current CREF test. Test I-57 involves three A-429M samples of an early experimental formulation. The test temperature was maintained in the range 150-155°F. Two of the three samples were cured at 250°F/15 hr; the third, at 350°F/4 hr. The samples were irradiated at an intensity of five (5) equivalent suns. Spectral reflectance measurements were made before irradiation (in air and in vacuum), after 100, 500, 1000, 1500 and 2000 ESH at a pressure of less than  $5 \times 10^{-7}$  Torr, and finally in air.

In the current CREF test (No. 9) the A-429M sample is being irradiated at room temperature at a solar ultraviolet radiation equivalent intensity of four (4) suns. Thus far spectral reflectance measurements have been made initially and after exposures of 575, 2000 and 3000 ESH. In this test the sample is from a more recent formulation.

#### 6.3.2 Results

The spectral reflectance curves for one of two 250°F/15 hr A-429M samples are shown in Figure 27; the spectra for the 350°F/4 hr sample are similar, but indicative of even greater stability. The CREF curves are shown in Figure 28.

The extraordinary performance of this paint system is markedly evident, especially in I-57 where an unusually severe temperature environment is maintained. Furthermore, despite the fact that these coatings have not been optimized, their reflectance values

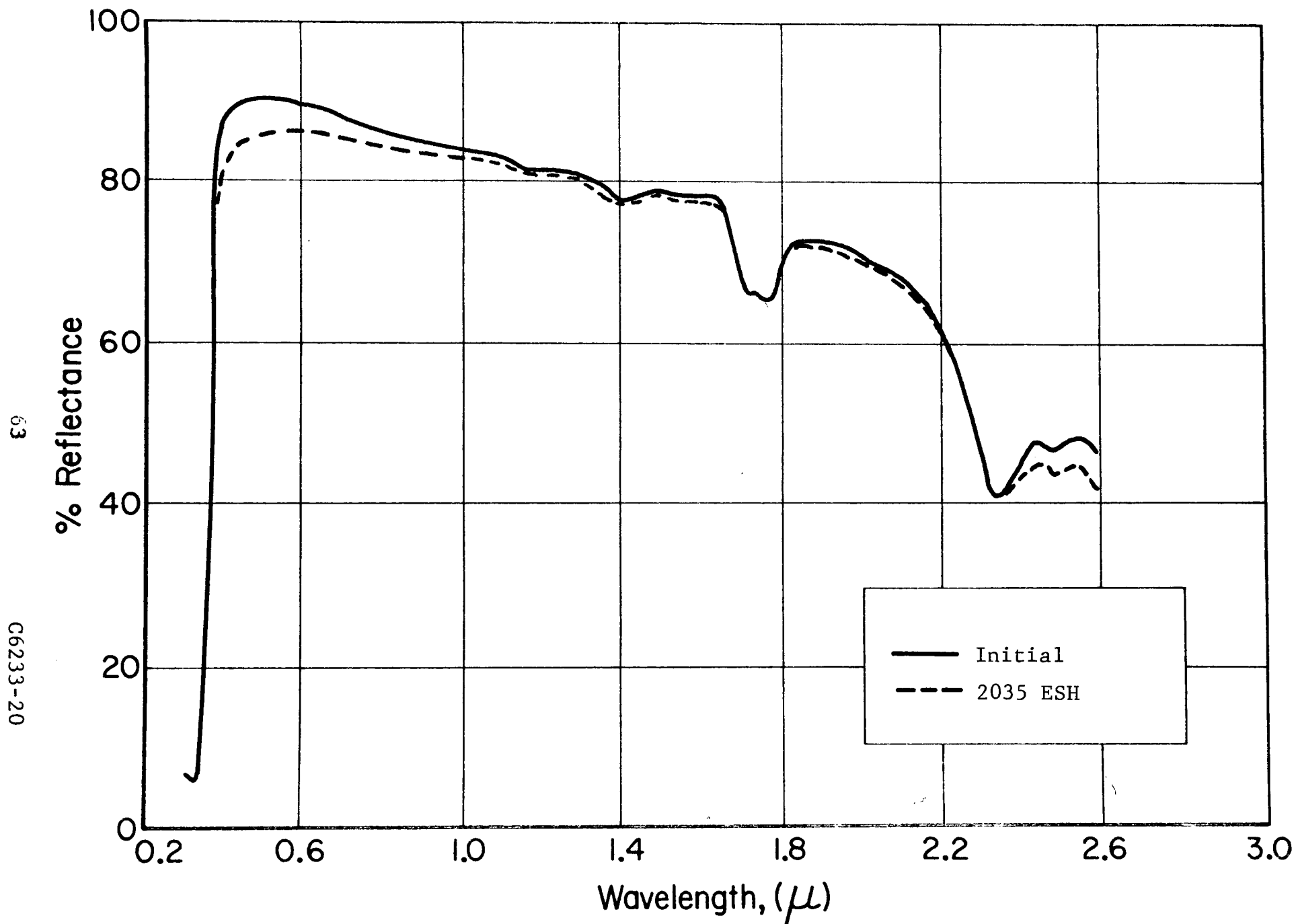


Figure 27 SPECTRAL REFLECTANCE OF IITRI'S A-429M:ZnO(SiO<sub>3</sub>)/OI-650G

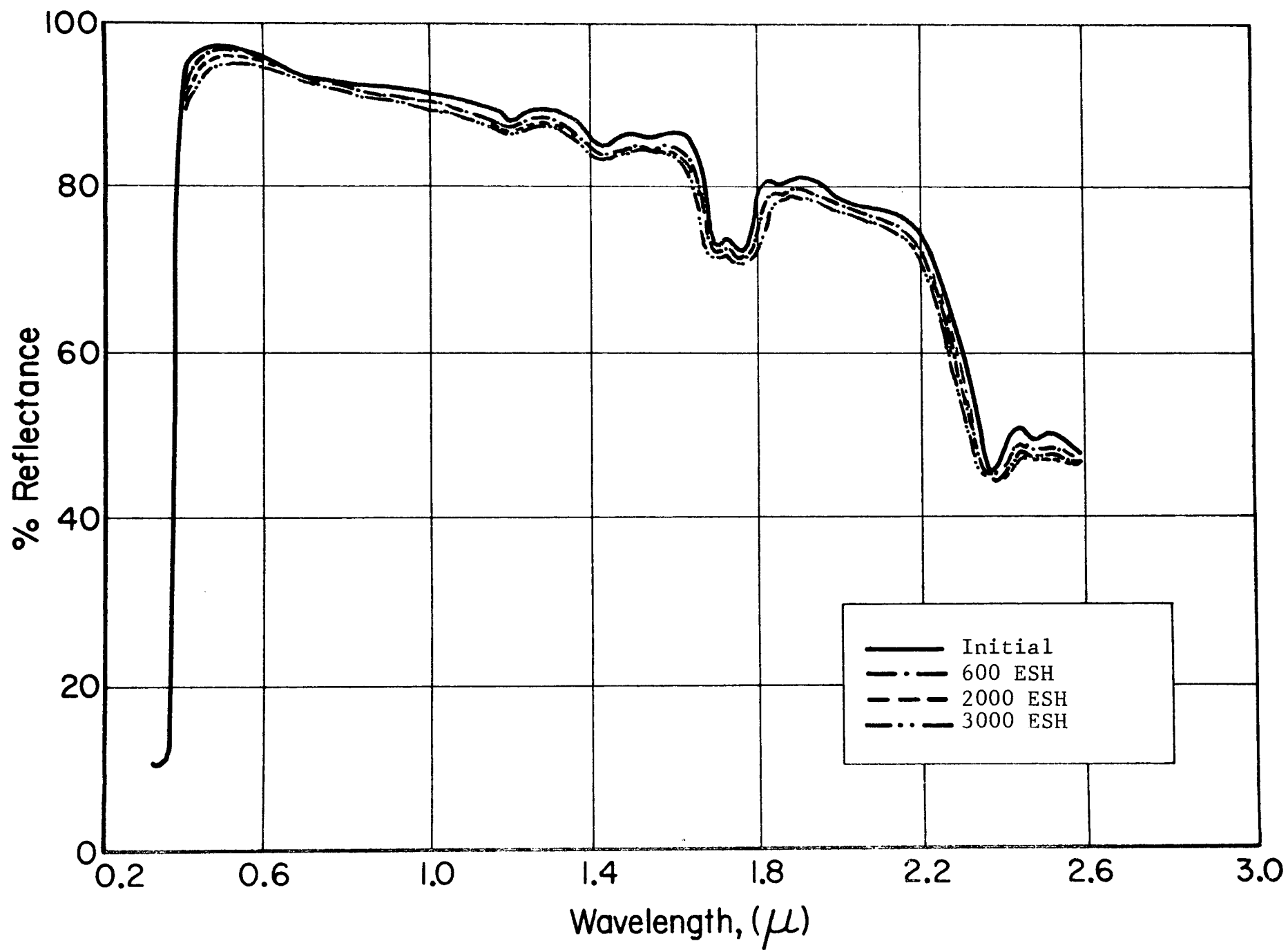


Figure 28 SPECTRAL REFLECTANCE OF IITRI'S A-429M: ZnO(SiO<sub>3</sub>)/OI-650G



are quite good. These two statements can be summarized quantitatively by noting that the solar absorptance in I-57 increased by only 0.018:0.204 to 0.222 in 2000 ESH.

In the current CREF ultraviolet irradiation test (No. 9), an A-429M sample continues to demonstrate very high stability. In more than 3000 ESH, the solar absorptance has increased by only 0.014. The spectra in this case suggest that the damage has saturated and that the solar reflectance has thus stabilized.

### 6.3.3 Conclusions

A-429M is undoubtedly the most stable paint system ever developed by IITRI and available in quantity. Its stability considerably exceeds that of S-13G and is superior even to that of Z-93. Its optical and engineering properties have yet to be optimized, but its performance patently qualifies it as a prime developmental goal.

## 7. SUMMARY

The quest for an ultra-stable, low solar absorptance/high emittance spacecraft thermal control coating system has in this program concentrated on the development of the zinc orthotitanate/Owens-Illinois 650 glass resin system. Methods of stabilizing these components individually have been successful, but a serious pigment-vehicle interaction remains a major impediment to the eventual deployment of this system in the field.

The development of space-stable zinc orthotitanate as a practical pigment involves, first, the development of a large scale production method with sufficient process control to assure high reproducibility and product quality, and, second, the development of a treatment scheme - encapsulation, heat treatment, etc. - which completely stabilizes the pigment surface and effectively prevents the pigment-vehicle interaction. Understanding the ultra-violet-induced mechanisms that operate on the pigment surface and in its bulk to create optical absorption is therefore an important key to the solution of this enigmatic phenomenon. The analyses of irradiation test results, however, are proving fruitful and progress toward this intermediate goal is being made.

The ultimate goal in this program is the achievement of a practical paint system that possesses a very low solar absorptance (0.12-0.14) and exhibits essentially zero degradation in this property. The encapsulated zinc orthotitanate/OI-650G system holds far greater promise toward meeting this goal than any other system known to us. For the immediate future the A-429M system can be regarded as a partial fulfillment of that goal - a more stable successor or alternative to either S-13G or to Z-93. Barring unanticipated or previously unexperienced difficulties, the paint is sufficiently through the R&D stage and engineering development is now warranted.